THE ANALYST

EDITORIAL

Congress on Modern Analytical Chemistry in Industry
St. Andrews, June 24th to 28th, 1957

MODERN Analytical Chemistry in Industry, the subject of the Congress organised by the Scottish Section and held in St. Andrews in June, attracted many more applicants than there was room for. Indeed, if success be measured by such criteria, no Congress could succeed better, for 299 Registered Members attended, at least seventy applications for registration were refused, and the very early announcement of the closure of registrations prevented an estimated two or three hundred further applications from being made. Even with this hard-hearted restriction of the numbers, the lecture theatre was always over-full, with seats in the aisles and on the platform occupied all the time.

The keynote of the Congress was the service that analytical chemistry provided for industry; and not only for chemical industry, but for industry as a whole. To provide this service efficiently, modern methods, techniques and apparatus were superseding the old, which were usually laborious and in the long run expensive. In opening the Congress, Dr. Pyke, the Scottish Section Chairman, pointed out that trained and experienced eyes matching Nessler tubes had been replaced by spectrophotometers operated by young girls and requiring only supervision by qualified analysts; eventually completely automatic analytical and recording apparatus would become commonplace in many branches of industry. Throughout the ensuing week, speaker after speaker showed in detail what could be done, and what had been done in many key industries, towards this end: many showed how results that could not have been produced a decade ago were now readily available by the use of new techniques, and nearly all showed how the increase in instrumentation had brought about increased accuracy, very often accompanied by a reduction in cost per analysis despite the initial capital expense of installing the instruments.

Much could be said of the diversity of interests of those attending the Congress—they came from all types of industry and from many countries, and over half were not members of the Society—but all attended practically every lecture. Perhaps it would be fairer to stress their unity of purpose—to learn of the progress being made in this fast-growing branch of science, analysis in its broadest sense. Indeed the packed lecture theatre spoke volumes for the interest aroused by the lecturers, and for the care with which the organisers had selected the topics. There are many counter-attractions in St. Andrews: golf, of course—and putting on "The Himalayas"; swimming, probably in The Step Rock Swimming Pool; talking with people and walking (along The Scores to the Cathedral and St. Rule's Tower) with people; and a host of other activities both in and outwith Permitted Hours. Informal contact and private activity form an important part of any Congress; they supplement the lectures and cannot be replaced by any formal gathering.

Not that the Social programme was neglected. Of necessity, with the restricted accommodation available, the number of members' wives present was not great, but coach trips to local places of interest were arranged for those not attending lectures, and the evenings were pleasantly occupied by a reception by the Congress chairman and committee, a cocktail party and the Congress dinner; a special performance at the Byre Theatre of "The Play's the Thing" and a private party for chairmen, lecturers and speakers completed the formal entertainments, but there were other less formal gatherings.

No Congress is complete without its exhibition, and, with its accent on instrumentation, this Congress was well supported by the manufacturers. Twelve industrial firms exhibited products and apparatus, and the U.K. Atomic Energy Authority's Research Group also took a stand. The exhibition was open every day, and Monday afternoon was especially set aside as a time of general viewing.

The organising committee had obviously worked well under its Chairman, Dr. Pyke, and mention must be made of Mr. J. Brooks, in whose special charge was the social programme, and Mr. A. F. Williams, who had special care of the scientific programme. The Congress Secretary, Mr. J. A. Eggleston—who is also the Scottish Section's Honorary Secretary and Treasurer—crowned his hard preparatory work by being ever-watchful that nothing should go awry. Other members of the Scottish Section Committee acted as hosts in the Halls of Residence, where most of us were accommodated.

To the University of St. Andrews we tender our sincere thanks for generous hospitality among such venerable surroundings. The modern equipment exhibited in the laboratories would undoubtedly have appeared strange to the fifteenth-century founders of St. Salvator's College, but the historic fabric of the Collegiate Church and the fifteenth-century maces signifying the College's authority added beauty and dignity to the scholastic atmosphere.

The lectures, papers and discussions will be published later by the Society in a bound volume. But in the meantime an excellent service has been rendered to the community by our contemporary, *Chemical Age*, in publishing extended summaries of the papers and accounts of the discussions and the general activities: part appeared during the Congress, copies being available on the last day, and the balance appeared the following week.

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

WESTERN AND MIDLANDS SECTIONS

A JOINT Summer Meeting of the Western and Midlands Sections was held at the Queen's Hotel, Cheltenham, on Friday, May 31st, and Saturday, June 1st, 1957.

The Chairman of the Western Section, Mr. P. J. C. Haywood, B.Sc., F.R.I.C., presided over the meeting at 6.30 p.m. on Friday, at which the following paper was presented and discussed: "Recent Advances in the Analysis of Plastics," by J. Haslam, D.Sc., F.R.I.C.

The Chairman of the Midlands Section, Dr. R. Belcher, F.R.I.C., F.Inst.F., presided over the meeting at 9.30 a.m. on Saturday, at which the following papers were presented and discussed: "The Analysis of Titanium, Zirconium and their Alloys," by W. T. Elwell, F.R.I.C.; "The Analysis of the Rarer Elements of Group III," by A. R. Powell, F.I.M., F.R.I.C., F.R.S.

At 3 p.m. on Saturday a visit was made to the Dowty Group Headquarters, Arle Court. Hydraulic equipment for aircraft, mining and fuel systems was displayed.

Determination of Indium in Rocks and Minerals by Radioactivation*

By A. A. SMALES, J. van R. SMIT and H. IRVING

Neutron-activation analysis has been applied to the determination of traces of indium, use being made of both the radionuclides indium-114 and indium-116. The ultimate sensitivity with irradiation in the Harwell Pile and use of 49-day indium-114 is 8×10^{-10} g. When there are facilities for chemical processing shortly after irradiation, it is possible to exploit the greater sensitivity of 5×10^{-12} g afforded by the 54-minute isomer indium-116. The radiochemical separations after the addition of carrier were based mainly on precipitations of indium as hydroxide and sulphide, together with stages of solvent extraction. Radiochemically pure indium was finally precipitated and counted as the tris-oxinate; the chemical yield was determined gravimetrically.

It was found to be essential to use dilute aqueous solutions of indium in the standards irradiated simultaneously with the analytical samples to avoid errors due to self-shielding, which were shown to be serious when standards of indium foil were used.

The method has been applied to the determination of indium in the standard rock samples G1 and W1, and in a number of separated minerals.

Indium is a "rare element" in the sense that no part of the world can be described as being especially rich in indium minerals, and only a very few minerals containing more than 0·1 per cent. of this element have been reported. As a typically dispersed element,[1] it enters into the composition of many rock-forming minerals and its over-all abundance in the earth's crust has recently been estimated as 0·11 p.p.m.[2,3] Hitherto, analyses have depended almost entirely on spectrographic methods, whose sensitivity is normally sufficient only to determine indium in the richest samples. With a double d.c. arc procedure, whereby a fractional distillation increases the sensitivity for such a readily volatile element as indium, and with tin as an internal standard, Shaw[2] found a sensitivity limit of 0·02 p.p.m., with a standard deviation of ± 20 per cent. for duplicate analyses on 400-mg samples.

There is clearly a need for an independent method of determining trace amounts of indium to check the results of such spectrographic procedures. It would need to be more sensitive than these if trends in the crustal distribution of indium are to be established at levels below 0·1 p.p.m., and if the more subtle and fundamental factors governing the geochemical associations of this element are to be established with any certainty.[4]

Feasibility of the radioactivation method—

The nuclear characteristics involved in the determination of indium are shown in Table I.

Table I

Nuclear data for indium

Target nuclide	Abundance in natural element, %	Isotopic activation cross-section, barns	Product on neutron irradiation	Radiation and energy, MeV	Half-life
^{113}In	4·23	61	^{114m}In	I.T., 0·192	49 days
		2	I.T. ↓ ^{114}In	β^-, 1·98	72 seconds
^{115}In	95·77	145	^{116m}In	β^-, 1·00 γ, 1·27, 1·09 2·1, 1·5	54·0 minutes
		52	^{116}In	β^-, 3·3	13 seconds

The irradiation of indium-113 produces simultaneously two nuclear isomers. Indium-114*m* decays with a half-life of 49 days to the lower-energy isomer indium-114. Secular

* Presented at the XVth International Congress on Pure and Applied Chemistry (Analytical Chemistry), Lisbon, September 8th to 16th, 1956.

equilibrium is rapidly established, after which the concentration of the 49-day indium-114 is measured by the 1·98-MeV β^- emission from the 72-second daughter. There is, however, no genetic relationship between the 13-second and the 54-minute nuclear isomers formed simultaneously by the neutron irradiation of indium-115. But after a few minutes the short-lived activity will have decayed away and the activity will be due entirely to the γ and β^- emission from the 54-minute isomer indium-116.

It can be calculated[5] that on irradiation in a flux of 10^{12} neutrons per sq. cm per second for one half-life (approximately 1 hour), 1 μg of indium will give $2{\cdot}2 \times 10^7$ disintegrations per minute. If a counting efficiency of 10 per cent. and a lower limit of detection of 10 counts per minute above background are assumed, the ultimate sensitivity for indium when the radionuclide indium-116 is used is 5×10^{-12} g. The decay occurring during the time required for chemical separation (say 3 hours) will reduce this by a factor of about 8. This great potential sensitivity for the analysis of indium by neutron activation equals that predicted for iridium, manganese and rhenium, and is only exceeded by that for gold and the rare earths lutetium, europium, dysprosium, and by that for the less common and naturally radioactive elements actinium, astatine, francium, polonium, radon and radium.[5]

With longer irradiations the contribution that 49-day indium-114 makes to the total activity becomes increasingly important, and after a period of cooling exceeding about 10 hours the whole of the activity will be due to this nuclide. Irradiation of 1 μg of indium for 2 weeks at a flux of 10^{12} neutrons per sq. cm per second would give $1{\cdot}4 \times 10^5$ disintegrations per minute due to indium-114. Losses due to the decay of indium-114 are smaller in this case and, if chemical separation is carried out after cooling for 1 week, an ultimate sensitivity of 8×10^{-10} g of indium should be possible.

When there are no facilities for chemical processing shortly after neutron irradiation, the great potential sensitivity offered by working with the 54-minute indium-116 cannot be fully exploited. But, even when it is only possible to work with the longer-lived isotope, satisfactory measurements can be made with a 400-mg sample containing no more than 0·002 p.p.m. of indium. With indium-116, radioactivation analysis should detect 0·002 p.p.m. even in a 20-mg sample. Both indium-114 and indium-116 were used in the work described in this paper.

Experimental

Irradiation—

Finely ground samples were sealed in short lengths of polythene tubing and packed, together with aluminium foil, into standard 3-inch × 1-inch aluminium cans for irradiation in the "self-serve" position in the Harwell Pile, usually for periods of 1 hour. Irradiation for shorter periods of between 1 second and 30 minutes were performed with the aid of the "rabbit," a pneumatic device for injecting samples into the Pile and withdrawing them very quickly. When the period of irradiation exceeded 5 days, as in analyses with indium-114, solid samples were sealed in silica ampoules of diameter 4 to 6 mm.

Standards—

Dilute aqueous standard solutions of indium in *M* nitric acid were sealed in silica ampoules with an internal diameter of 4 mm, for simultaneous irradiation with the analytical samples. Preliminary work had shown that a considerable error could be introduced if solid standards of indium foil were used, owing to the large "self-shielding" effect (see p. 547). There is no suitable compound of indium of accurately known composition to simulate the dispersion of indium through a solid matrix. Although up to 15 per cent. of indium is soluble in molten aluminium at 660° C, it is almost insoluble in the cold. But the attractive possibility of using dilute alloys of indium in aluminium as solid standards is vitiated by uncertainties as to their ultimate homogeneity.

If aliquot portions of a dilute standard solution of indium are treated with a drop of detergent (1 per cent. solution of Teepol), and evaporated to dryness under an infra-red lamp on 4-cm × 4-cm squares of aluminium foil, reproducible thin standards result. Three samples prepared in this way and irradiated for 10 days gave specific activities of 14,240, 14,240 and 14,340 counts per minute per μg. A blank determination showed that the indium content of the foil was negligible. Preference was given, however, to standards prepared from weighed amounts of a dilute solution of indium.

CHEMICAL SEPARATION—

Meinke and Anderson[6] explored the possibility of using low-level neutron sources for the determination by radioactivation of indium as indium-116, but counted all samples without any chemical treatment. Hudgens and Nelson[7] determined by radioactivation small amounts of indium added to aluminium oxide and aluminium sulphate, with use of a stage of solvent extraction in the chemical separation. They separated indium as its hydroxide for counting as indium-116, and subsequently ignited this to In_2O_3 to determine the chemical yield. However, it has been shown that a precipitate of indium hydroxide readily carries down traces of metals normally soluble in ammoniacal solution.[8,9]

More elaborate procedures involving cycles of "scavenging" precipitations and the use of hold-back carriers have been described for separating indium activity from specific cyclotron-target materials, *e.g.*, cadmium,[10,11] antimony[12] and uranium,[13,14] and for the isolation of active indium from mixed fission products.[15,16] However, no radiochemical methods have been published for isolating indium activity from irradiated rock samples or from mixtures of similar nature and complexity. In the present work, cycles of scavenging precipitations were used in conjunction with known differences in the solvent extraction of metal halides,[17,18] to secure the necessary "decontamination" of indium from a large number of other elements, notably iron. Fifteen milligrams of inactive indium were added as carrier and the radiochemically pure element obtained from the chemical separation was precipitated for counting as the tris-oxinate. The chemical yield was determined gravimetrically on the dry oxine complex; it was usually about 50 per cent.

MEASUREMENT OF RADIOACTIVITY—

The final precipitate of indium tris-oxinate was counted under an end-window counter of the EHM 2 type, associated with an automatic sample changer and a print recorder, which registered for each measurement the number of the sample-holder, the (pre-set) duration of the count, the total number of counts and the cumulative time of counting. A statistical accuracy of 0·5 per cent. was achieved by timing 40,000 counts when possible. When the activity was low, however, counting was done for a period of 60 minutes. An external quenching circuit with a dead-time of 400 microseconds was employed, and all counts were corrected for coincidences and for background.

In view of the high β-energy of indium-114 (1·98 MeV), errors due to self-absorption were not expected. Self-scattering effects might nevertheless cause the measured activity to be a function of the weight of inactive carrier present such that the graph of counting rate against sample weight (for a fixed amount of activity) would pass through a maximum.[19] To check this, a constant amount of indium-114 tracer was mixed with increasing amounts of indium carrier and the precipitation, mounting and counting of the tris-oxinate was carried out by a standard procedure. The activities of the samples after correction to 100 per cent. chemical yield are shown in the last column of Table II. The absence of any definite trend shows that no correction for self-absorption or self-scattering need be made. These results also indicate the order of reproducibility of the over-all procedure.

TABLE II

COUNTING RATE OF A FIXED AMOUNT OF INDIUM-114 ACTIVITY WITH DIFFERENT WEIGHTS OF INDIUM OXINATE

Inactive indium taken, mg	Indium oxinate calculated, mg	Indium oxinate found, mg	Measured activity, counts per minute	Corrected activity, counts per minute
2	9·34	5·4	3673	6350
3	14·0	10·4	4658	6275
4	18·7	14·1	4802	6360
5	23·3	17·8	4890	6395
6	28·0	25·0	5603	6275
8	37·3	33·9	5835	6415
10	46·7	42·7	5704	6245
12	56·0	46·4	5175	6250
14	65·4	49·4	4802	6355
15	70·0	64·9	5854	6320
				Mean = 6324 ± 58

Decay curves were determined for all samples containing 54-minute indium-116 to establish their radiochemical purity, and absorption curves were taken when working with indium-114. Typical examples are shown in Figs. 1 and 2.

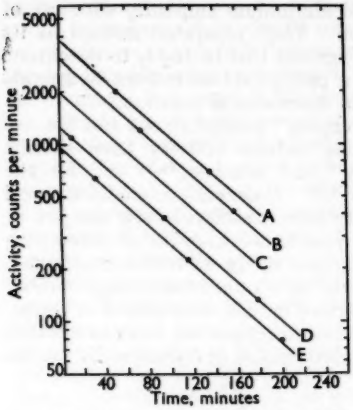

Fig. 1. Analysis of EG 4327 samples (Table IV) by the indium-116 method: curves A and B, indium activity of standards; curve C, line of slope corresponding to a nuclide with a half-life of 54 minutes; curves D and E, indium activity separated from irradiated samples

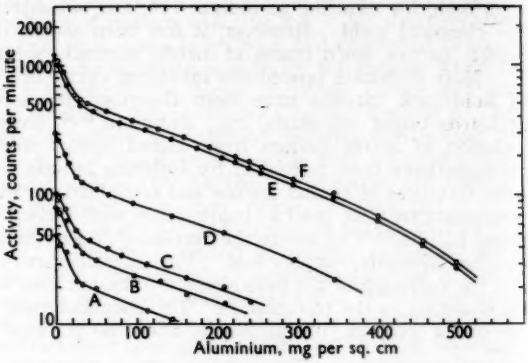

Fig. 2. Aluminium-absorption curves for separated indium-114 activity: curve A, sample EG 1825 (Table IV); curve B, sample EG 4328 (Table IV); curve C, sample EG 4327 (Table IV); curve D, cylindrite[27]; curve E, indium standard; curve F, cylindrite[27]

Method

Reagents—

Dilute standard indium solution—Prepare a solution containing 15 mg of Specpure indium wire in 1 litre of *M* nitric acid.

Indium carrier solution—Dissolve 1·5 g of pure indium metal in dilute hydrochloric acid and dilute to 500 ml.

1 ml ≡ 3 mg of In.

Copper carrier solution—Prepare a solution of cupric chloride in 0·5 *M* hydrochloric acid containing 10 mg of copper per ml.

Iron carrier solution—Prepare a solution of ferric chloride in 6 *M* hydrochloric acid containing 10 mg of iron per ml.

Nickel and barium carrier solutions—Dissolve the appropriate weight of the respective chlorides in water to give solutions containing 10 mg of nickel (or barium) per ml.

Oxine solution, 5 per cent.—Dissolve 5 g of 8-hydroxyquinoline in 100 ml of 96 per cent. ethanol.

Acetate buffer solution—Dissolve 272 g of trihydrated sodium acetate in distilled water, add 60 g of glacial acetic acid, and dilute to 1 litre.

Sodium peroxide, powdered.

Hydrochloric acid, sp.gr. 1·18.

Perchloric acid, 72 per cent.

Sodium hydroxide solution, 20 per cent.

Hydrobromic acid, 46 to 48 per cent.

Ammonia solution, sp.gr. 0·880.

Sodium sulphite solution—A saturated solution in water.

Procedure for indium-114—

Prepare irradiation ampoules about 5 cm long from silica tubing with a diameter of 5 to 6 mm (or an internal diameter of 4 mm for the standards), each having a constriction near the open end. Grind the sample until it passes through a 300-mesh sieve and weigh

out accurately about 0·5-g portions into each ampoule. Prepare standards by weighing out 0·1 to 0·2 ml of the dilute standard indium solution. Seal off the ampoules and pack them into a standard aluminium can with aluminium foil. Each irradiation unit should contain two standards with four or more samples, which should be prepared in duplicate. Irradiate for at least 7 days, and then allow the can to "cool" behind a radiation shield for one-half of the irradiation period.

Remove the ampoules from the can, open them at the constriction, and transfer the solid samples to silica crucibles. To each add 3 to 4 g of powdered sodium peroxide and mix thoroughly. Finally, cover the mixture in each crucible with a thin layer of sodium peroxide and heat in an electric muffle furnace at 480° to 500° C for 10 to 15 minutes. Remove the crucibles from the furnace and quickly cool them by immersing their outside walls in a beaker of water. Detach the cake from each crucible and transfer it to a 150-ml beaker covered with a watch-glass. Dissolve the melt carefully in about 200 ml of water and acidify with hydrochloric acid, sp.gr. 1·18.

Mineral samples that resist the attack by sodium peroxide and samples of pure ilmenite and magnetite were taken up by fusion with four times their weight of potassium hydrogen sulphate.

Stages in the chemical separation that now follows are numbered to facilitate reference in subsequent discussion—

(1) To the acidified solution add an accurately known weight (15 mg) of indium carrier solution. Add 10 mg of nickel carrier solution and boil for 1 minute.

(2) Transfer the solution to a 50-ml centrifuge tube and precipitate the hydroxides by adding an excess of ammonia solution. Spin, and discard the supernatant liquid.

(3) Dissolve the precipitate in 10 ml of 72 per cent. perchloric acid and transfer back to the original beaker. Evaporate under an infra-red lamp until copious fumes appear. Add a further 2 ml of perchloric acid and continue heating for 20 minutes.

(4) Take up the residue as completely as possible in hot water and filter into the original centrifuge tube. Wash the precipitate thoroughly with hot water and discard it. To the combined filtrate and washings add sodium hydroxide solution in excess. Spin the precipitated hydroxides in a centrifuge and discard the supernatant liquid. Dissolve the precipitate in dilute hydrochloric acid and add 2 ml of saturated sodium sulphite solution. Add excess of ammonia solution and spin in a centrifuge.

(5) Dissolve the precipitate in 11 ml of 46 to 48 per cent. hydrobromic acid (about 8·5 *M*) and dilute with 9 ml of water to give 20 ml of approximately 4·5 *M* hydrobromic acid solution. Transfer to a 100-ml separating funnel and extract the indium by shaking with two 25-ml portions of diethyl ether. Run off and reject the aqueous phase. Wash the combined ether phases by shaking with two 5-ml portions of freshly prepared 4·5 *M* hydrobromic acid. Reject the aqueous washings.

(6) Extract the indium from the ether phase by equilibrating with three successive 5-ml portions of 6 *M* hydrochloric acid. Discard the ether phase. Wash the combined aqueous extracts once with 15 ml of ether and reject this. To the solution in hydrochloric acid add 10 mg of iron carrier solution and extract with two 15-ml portions of ether. Reject the ether phases. Add a further 10 mg of iron carrier solution to the hydrochloric acid solution and extract with three 15-ml portions of ether, again rejecting the ethereal phases.

(7) To the aqueous phase add ammonia solution until indium hydroxide starts to be precipitated, and then add 10 mg of copper carrier solution, which should give a deep blue colour. Add concentrated hydrochloric acid dropwise until the blue colour fades, and then add 1 ml of hydrochloric acid, sp.gr. 1·18, and dilute to 25 ml. The acidity at this stage should be about 0·5 *M*. Heat to 60° C and saturate with hydrogen sulphide. Filter off and discard the precipitate. Collect the filtrate and boil it to remove hydrogen sulphide.

(8) To the hot filtrate add 10 mg of copper carrier solution and saturate at 60° C with hydrogen sulphide. Filter off and discard the precipitate.

(9) Repeat step (8) once.

(10) To the filtrate from step (8) add about 2 g of solid ammonium acetate, heat to 70° to 80° C and saturate with hydrogen sulphide. Spin in a centrifuge and reject the supernatant liquid.

(11) Dissolve indium sulphide from the precipitate by adding 12 ml of cold *M* hydrochloric acid and triturating with a glass rod. Filter off and discard any insoluble residue.

(12) Repeat steps (10) and (11) once.

(13) Boil the solution of indium in hydrochloric acid for 1 minute to expel hydrogen sulphide and then add 10 mg of barium carrier solution. Make the solution ammoniacal and spin the precipitated hydroxides in a centrifuge. Reject the supernatant liquid.

(14) Dissolve the precipitated indium hydroxide in 4 drops of concentrated hydrochloric acid, dilute to 15 ml and add 2 ml of oxine solution. Heat to 50° to 60° C and precipitate indium oxinate by the slow addition of 5 ml of acetate buffer solution. Spin in a centrifuge and wash the precipitate twice with hot 5 per cent. ethanol, using a glass rod to break up the precipitate if necessary. Make a slurry of the precipitate with a small amount of water and transfer with a drop-pipette to a tared aluminium counting tray. Dry under an infra-red lamp, cool, and weigh to determine the chemical yield.

At a convenient time open the ampoules containing the irradiated indium standards. Using a drop-pipette drawn out to a point, transfer the indium solution quantitatively to a 100-ml calibrated flask and rinse thoroughly with hot 2 *M* hydrochloric acid. The final concentration of acid is immaterial. Cool, and dilute to the mark. Transfer a suitable aliquot, depending on the amount of indium expected in the sample, to a 50-ml centrifuge tube and add exactly the same weight of indium carrier (15 mg) as in the chemical separation described above. After thorough mixing, precipitate the indium with an excess of ammonia solution. Spin in a centrifuge and reject the supernatant liquid. Re-dissolve the precipitated indium hydroxide in 4 drops of concentrated hydrochloric acid and then precipitate indium oxinate; mount, dry and weigh it as described in step (14).

PROCEDURE FOR INDIUM-116—

Amounts of up to 150 mg of finely powdered sample (less than 300 mesh) are used in this procedure. After introduction of a known weight into a short length of polythene tubing with an internal diameter of 3 to 4 mm, the free end was sealed by being heated in a small flame and squeezed with a pair of tweezers. Liquid samples were prepared as before by weighing out known amounts of dilute indium standard solution into silica ampoules. Since the entire chemical separation and subsequent counting must be carried out with the greatest expedition, only two samples and one standard are packed into an aluminium can and are irradiated for 1 hour, by which time the activity due to indium-116 will have reached about one-half of its saturation value. Samples and standard are processed after "cooling" for 30 to 40 minutes.

The chemical procedure for isolating indium-116 activity is essentially the same as that already described for indium-114. But, since the total weight of sample is smaller, stages (3) and (4) may be omitted. These stages are designed to render insoluble any silica that may accompany the hydroxide precipitate from the preceding stage. When working with larger sample weights, it was found that silicic acid from stage (2) dissolved freely in concentrated hydrobromic acid, but separated at the interface on subsequent dilution and equilibration with ether in stage (5). Under these conditions phase separation was delayed and a clean separation could only be achieved by prolonged centrifugation. A further simplification arises from the smaller contribution made by iron-59 to the total activity when the time of irradiation is short, as is so with the indium-116 procedure. For samples of comparable iron content, the indium-116 procedure permits of a lower decontamination from iron and usually one scavenging with iron carrier is sufficient. With this modification stage (6) would read—

(6) Extract the ether phase by equilibrating with three successive 5-ml portions of 6 *M* hydrochloric acid. Discard the ether phases. Wash the combined aqueous phases twice with 15 ml of ether. To the hydrochloric acid solution add 10 mg of iron carrier solution and extract with three 15-ml portions of ether, again rejecting the ethereal phases.

With these exceptions the procedures for indium-114 and indium-116 are identical. The irradiated standard is transferred quantitatively as before to a 100-ml calibrated flask and made up to the mark. But two aliquot portions are taken and precipitated with indium carrier. In view of the rapid decay of indium-116, the precipitates of indium oxinate were

counted immediately after mounting and the weighing of the dried samples to determine the chemical yield was postponed until after the counting had been completed.

With use of the automatic sample changer, the activity separated as indium oxinate for each analytical sample was counted at least three times, and that from the standards at least twice, for periods of 20 to 30 minutes in each instance. With a counting interval of less than half the half-life of a nuclide, the disintegration rate may be assumed to equal the activity at the mid-point of the duration of the count. Since the printing mechanism records the total accumulative time at the completion of each individual count, a plot of of the logarithm of the counting rate against the difference between the registered accumulative time and half the counting interval gave points on the decay curve for the separated nuclide. The experimental points, shown in Fig. 1, always lay on straight lines parallel to the theoretical decay curve for 54-minute indium-116 (Fig. 1, curve A), so confirming the radiochemical purity of the isolated indium. Extrapolation of these curves to zero time, or to any other arbitrary time, gave activity readings for sample and standards from which the indium content of the original material could be found from the relationship—

$$\text{Weight of indium in the sample} = \text{Weight of indium in standard} \times \frac{\text{Corrected counting rate of sample}}{\text{Corrected counting rate of standard.}}$$

Results

Uniform specimens of the granite G1 from Westerly, Rhode Island, and of the diabase W1 from Centerville, Virginia, prepared by Fairbairn *et al.*[20] as standards for both major and minor constituents of igneous rocks, were available. The indium contents of G1 and W1 were determined by radioactivation, both the indium-114 and the indium-116 procedures being used. The satisfactory agreement of the data by these two methods is shown in Table III.

Table III

Determination of the indium contents of W1 and G1 by neutron-radioactivation analysis

Sample	Method	Indium content, p.p.m.	Average indium content, p.p.m.
G1	^{114}In	0·024, 0·026	0·025 ± 0·001
G1	^{116}In	0·026, 0·025, 0·029, 0·029, 0·025, 0·026	0·026 ± 0·002
W1	^{114}In	0·064, 0·070, 0·061	0·065 ± 0·004
W1	^{116}In	0·065, 0·065, 0·062, 0·063	0·064 ± 0·003

Although a detailed study has been made of the distribution of a number of trace elements in the Skaergaard intrusion in East Greenland,[21] no data for indium are available, possibly because its concentration fell outside the limit of sensitivity of the spectrographic methods employed. A number of rock specimens from the Skaergaard complex (referred to by their collection numbers) were supplied by Prof. L. R. Wager of the Department of Geology, Oxford University, and analysed for indium by the two procedures detailed above. The results are summarised in Table IV, but the geochemical implications of these data are discussed elsewhere.[4]

Table IV

Indium content of rocks from the Skaergaard intrusion

Collection number	Method	Indium content, p.p.m.	Average indium content, p.p.m.
EG 1825	^{114}In	0·060, 0·062, 0·060	0·061 ± 0·002
	^{116}In	0·062, 0·062, 0·059, 0·062	0·061 ± 0·002
EG 4507	^{114}In	0·055, 0·052, 0·054	0·054 ± 0·002
	^{116}In	0·053, 0·058, 0·054, 0·056, 0·053, 0·054, 0·050, 0·053	0·054 ± 0·003
EG 4327	^{114}In	0·16(3), 0·17(0), 0·15(1)	0·16 ± 0·01
	^{116}In	0·16(4), 0·17(2), 0·16(7), 0·17(4)	0·16(9) ± 0·004
EG 4328	^{114}In	0·19(4), 0·16(4)	0·18 ± 0·02
	^{116}In	0·18(0), 0·18(3), 0·19(0), 0·17(4), 0·17(8), 0·18(7)	0·18(2) ± 0·00(6)
EG 3058	^{114}In	0·093, 0·089	0·091 ± 0·002
EG 5086	^{116}In	0·059, 0·062	0·060 ± 0·002

A preliminary examination of the distribution of indium in the ferrogabbro EG4327 was carried out on a 13-g sample. After being de-slimed by decantation with water and then washed with acetone and dried, the −300-mesh fraction ("fines") was screened off and the +300-mesh fraction was fed to a Franz iso-dynamic magnetic separator.[22] The indium content of various fractions, determined by the indium-116 method only, is reported in Table V.

TABLE V

INDIUM CONTENT OF VARIOUS FRACTIONS OBTAINED FROM A FERROGABBRO BY USING A MAGNETIC SEPARATOR

Approximate composition of fraction	Weight of fraction, g	Proportion of fraction by weight, %	Indium content (average of two determinations), p.p.m.	Indium content of fraction, g per ton (almost exactly ≡ p.p.m.)
Pure magnetite, with very little iron-rich silicates	0·34	3·7	0·090 ± 0·005	0·003
Magnetite - ilmenite, with rather more iron-rich silicates	0·51	5·6	0·150 ± 0·004	0·008
Very clean non-magnetic fraction, mostly feldspars	1·45	15·9	0·004 ± 0·001	0·015
Ilmenites and iron-rich silicates	0·68	7·4	0·19(4) ± 0·004	0·063
Similar to the preceding fraction, but less magnetic and perhaps less ilmenite	1·84	20·2	0·31(1) ± 0·00(8)	0·071
"Fines," unseparated fraction of −300 mesh	4·32	47·3	0·158 ± 0·005	0·071
Total for all fractions	9·14	100·0	—	0·161
Unseparated rock sample EG4327	—	—	0·17	—

The low figure obtained for the indium content of the feldspar fraction confirms the observations of Lundegårdh, who found that indium was generally completely absent from quartz and feldspar.[23] Indium does not appear to concentrate with iron in magnetite, but it would be unjustifiable to draw any more detailed conclusions from these results, since the composition of the various fractions was not evaluated mineralogically. Prof. Wager has since made available to us specimens of pure olivine, ilmenite, magnetite, feldspar and pyroxene that had been separated from sample EG 4327 by standard mineralogical techniques in the Department of Geology, Oxford University. Analyses of these minerals and of a number of pyroxenes by the indium-116 method will be reported elsewhere.[4]

INTERFERING ELEMENTS

NUCLEAR INTERFERENCE—

We must now consider possible errors caused by the presence in the sample to be irradiated of elements, other than indium, that, through nuclear reactions, might give rise to the nuclides indium-114 or indium-116 (or to any other radioactive isotopes of indium of similar characteristics) either directly, or by the intermediate formation of the stable isotopes indium-113 and indium-115. The elements antimony, tin and uranium demand detailed consideration.

Natural antimony consists of two isotopes, antimony-123, which occurs to the extent of 42·75 per cent., could give rise to indium-120 by an n,α reaction; but this isotope has never been identified. The more abundant isotope antimony-121 could give rise to the pure β-emitter indium-118 also by an n,α reaction; but the short half-life (4·5 minutes) of this nuclide would not introduce errors into the procedures involving indium-114 or indium-116.

If large amounts of tin were present, indium could be formed by the following reactions—

$$^{114}_{50}\mathrm{Sn} + {}^{1}_{0}n \longrightarrow {}^{114}_{49}\mathrm{In} + {}^{1}_{1}\mathrm{H} \quad (n,p)$$

$$^{116}_{50}\mathrm{Sn} + {}^{1}_{0}n \longrightarrow {}^{116}_{49}\mathrm{In} + {}^{1}_{1}\mathrm{H} \quad (n,p)$$

and

$$^{115}_{50}\mathrm{Sn} \xrightarrow{\gamma} {}^{114}_{49}\mathrm{In} + {}^{1}_{1}\mathrm{H} \quad (\gamma,p)$$

$$^{117}_{50}\mathrm{Sn} \xrightarrow{\gamma} {}^{116}_{49}\mathrm{In} + {}^{1}_{1}\mathrm{H} \quad (\gamma,p)$$

The exact cross-sections for these n,p and γ,p reactions are not known for conditions prevailing in the Pile. An estimate of the possible interference was, however, made by irradiating two samples of AnalaR tin metal (121·8 and 104·4 mg), together with suitable pure indium standards, in the Pile for 1 hour. The indium activity was separated as before and counted as indium-116. A decay curve corresponding to a half-life of 54 minutes identified the separated nuclide. The apparent indium content of the two samples was calculated to be 11·7 and 10·3 μg. It is very probable that a large proportion of the activity was derived from traces of indium present as impurity in the original sample of tin[24] and the maximum interference can be stated as 100 μg of indium per g of tin. Since igneous rocks usually contain less than 100 p.p.m. of tin,[25] the maximum correction from this cause would amount to 0·01 p.p.m. of indium.

Another possible mode of formation of indium nuclides is by the slow-neutron fission of uranium. Indium-117 has been identified among the products, but its half-life (117 minutes) differs sufficiently from that of indium-114 and indium-116 to permit it to be differentiated. Since the fission cross-section for this and any other process leading to indium is not known with certainty, the extent to which uranium might introduce errors in the radioactivation analysis of indium was examined experimentally.

Samples of Specpure U_3O_8 and the appropriate weights of pure indium standards were irradiated simultaneously for 30 minutes and allowed to "cool" for 1 hour. After the addition of 15 mg of indium carrier, the activity was isolated as before. Indium-117 (half-life 117 minutes) and indium-115 (half-life 4½ hours) are both daughters of cadmium produced in the uranium fission process. The separation of cadmium and indium during the procedure for separating the latter radiochemically pure occurred about 1½ to 2 hours after irradiation. The decay curve of the separated indium indicated the presence of small proportions of 54-minute and 4½-hour activities. The greater part decayed with the 117-minute half-life characteristic of indium-117. However, on the assumption that all the activity had been due to indium-116, the apparent indium contents of two samples of U_3O_8 (46·4 and 65·4 mg) were found to be 0·059 and 0·078 μg, respectively, *i.e.*, approximately 1·2 μg per g of U_3O_8.

To determine the extent of interference in the longer irradiations needed for the indium-114 procedure, two samples of U_3O_8 (115·1 and 125·2 mg) were irradiated with pure indium standards for 2 weeks. After the samples had "cooled" for 8 days, the indium activity was separated as usual, samples of indium oxinate being counted 48 hours after precipitation. Assuming in this instance that all the activity had been due to indium-114, the apparent indium contents of the two samples were 0·19 and 0·20 μg, respectively, *i.e.*, approximately 1·6 μg per g of U_3O_8. From both determinations it is clear that interference from uranium fission is likely to be very small and less than 2 μg of indium per g of natural uranium. Hence in a mineral, 1 p.p.m. of uranium could cause an error of 2×10^{-6} p.p.m. of indium, and for a mineral containing even 0·1 per cent. of uranium, the maximum correction in the indium determination would not be more than 0·002 p.p.m.

Chemical interference—

The methods described in which indium-114 and indium-116 are used are applicable to a wide variety of specimens, although in some determinations the need might arise for extra decontamination steps in the chemical procedure. The need for such extra steps will be apparent from the decay and absorption curves (compare with Figs. 1 and 2), and it is usually a simple matter to design additional chemical steps for the removal of the contaminant. Thus, in preliminary experiments high results for G1 were obtained by the indium-114 method (0·039, 0·040, 0·032 and 0·049 p.p.m.) as compared with lower and more consistent results obtained by the indium-116 method (0·025, 0·025 and 0·026 p.p.m.). Aluminium-absorption curves revealed radiochemical contamination that was identified as due to iron-59, and in consequence the procedure described in this paper now includes additional stages of scavenging for iron.

Self-shielding—

When indium foil of thickness 0·0051 cm was used to prepare standards for simultaneous irradiation with rock samples, the indium content of the latter always appeared to be 30 to 40 per cent. lower than when dilute solutions of indium were used. That this was due to self-shielding effects was clearly shown by the differences between the measured specific activity of samples of indium foil of different dimensions irradiated simultaneously; but the

magnitude of the discrepancies was too large to be accounted for by the accepted value of 190 barns for the total cross-section of indium for thermal neutrons. However, the flux in the irradiation positions of the Harwell Pile has a proportion of neutrons of higher than thermal energy, and the neutron-absorption spectrum of indium[26] shows very high resonance peaks in the energy range 1·0 to 10 MeV, where the atomic capture cross-section rises to a maximum of about 30,000 barns. Since the self-shielding effect may be calculated from the expression—

$$f = f_0 e^{-nx\sigma},$$

where f is the flux of neutrons per sq. cm per second, at a distance x cm from the surface, σ is the capture cross-section of the material in sq. cm and n is the number of atoms per cubic cm, the effect will be greatly enhanced if resonance neutrons, even in small proportion, appear in the neutron spectrum of the Harwell Pile. An estimate of this was made by irradiating simultaneously for 100 seconds one sample of pure indium foil (13·4 mg) and a second sample that had been wrapped in cadmium foil 0·015 cm thick. Since cadmium has a capture cross-section of about 20,000 barns for thermal neutrons, it can be calculated that the flux of thermal neutrons reaching the wrapped sample is less than 10^{-6} of that reaching the other. Cadmium is, however, effectively transparent to non-thermal neutrons. Since the specific activities of the two irradiated indium specimens were 1903 and 1105 counts per minute per μg, it appears that more than 50 per cent. of the activity (due to indium-114) is brought about by resonance neutrons. On this account errors due to self-shielding were minimised as far as possible by employing dilute solutions of indium as standards, even when long periods of irradiation in the Pile were necessary.

Conclusions

The methods described in this paper have been applied to samples containing amounts of indium as small as 3×10^{-9} g and the ultimate sensitivity of the method has not been approached. Precision (standard deviation) was generally better than ± 10 per cent. The low indium concentration in the standard granite and diabase, G1 and W1, has been established and the very low indium content of feldspar has been confirmed.

The major advantages of the present methods over the spectrographic methods previously used in studying the geochemical association of indium are greatly improved sensitivity and the avoidance of those errors inherent in emission spectrography, in which the standard curves cannot be prepared from known amounts of pure indium in matrices corresponding exactly in composition with that of the unknown sample.

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Determination of Indium in Cylindrite by Neutron-activation Analysis and other Methods

BY H. IRVING, J. VAN R. SMIT AND (IN PART) L. SALMON

Neutron-radioactivation analysis has been applied to the determination of indium in the rare sulphide mineral cylindrite. Radiochemical separations were required in two procedures in which 49-day indium-114 and 54-minute indium-116, respectively, were used. However, analysis of the decay curve of a sample of cylindrite that had been irradiated with neutrons (for 1 second only) permitted the determination of its indium content without any chemical separations, and these were also avoided by the use of gamma-ray spectrometry. The four methods gave results in good agreement, *viz.*, 0·146 ± 0·003, 0·141 ± 0·005, 0·15 ± 0·01 and 0·154 ± 0·003 per cent. of indium.

It has been shown, by using radiotracers, that no indium is lost under conditions in which tin and antimony can be volatilised quantitatively as their bromides, and that no indium is co-precipitated with lead from sulphuric acid solutions. With this knowledge the quantitative separation of indium from a 100-mg sample of cylindrite was achieved by a procedure that involved stages of solvent extraction with hydriodic acid, dithizone and 8-hydroxyquinoline. The final absorptiometric determination as the tris-oxinate complex gave a value for the indium content of cylindrite in good agreement with that found radiometrically.

UNTIL recent years, when indium has become available in large quantities as a by-product in the treatment of zinc, tin and lead ores,[1] the scarcity of this metal had greatly restricted the study of its chemistry, and in a search for richer sources of this widely dispersed element (for which a recent estimate of the crustal abundance is as low as 0·1 p.p.m.[2]), considerations of possible geochemical associations led Brewer and Baker[3] to examine a number of minerals containing tin and silver.

A specimen of the mineral cylindrite from the Sant Cruz mine, Poopo, Bolivia, showed exceptional promise, since a spectrographic determination with use of the most persistent indium lines at 3039 and 3256 A gave its indium content as 0·1 to 1 per cent. When, however, the determination was carried out after a preliminary separation of the indium in a 1-g sample, the lower figure of 0·1 per cent. was obtained.[4] Cylindrite is a sulphide of lead, tin and antimony, and contains approximately 21 to 26 per cent. of tin, 7 to 13 per cent. of antimony, 34 to 39 per cent. of lead, 24 per cent. of sulphur with up to 3 per cent. of iron, 0·6 per cent. or less of silver and a small variable percentage of silica. The difficult extraction of indium from this matrix was attempted with two large samples of 100 and 269 g of the crude mineral.[4] The yields of indium sulphide (0·0185 and 0·2048 g, respectively) indicated 0·013 and 0·054 per cent. as the lower limits for their indium content.

Since a small amount of the original sample of cylindrite was still available, it was decided to re-determine its indium content by the more sensitive methods of neutron-activation analysis described in the preceding paper.[5] These analyses were supplemented

by two other radioactivation procedures and an attempt has been made to carry out the determination of the indium absorptiometrically after removal of interfering elements.

Experimental

Procedure for indium-114—

As the cylindrite was expected to contain more than 1000 p.p.m. of indium, the methods already used successfully for rock samples containing 1 p.p.m. or less[5] could be modified by taking smaller samples, or by reducing the time of irradiation. The former alternative could introduce uncertainties caused by a possible lack of homogeneity in the specimen of cylindrite, whereas the latter alternative had the positive advantage of reducing interference from elements that give rise to nuclides of comparable or longer half-life than that of the indium nuclide used for measurement.

Well formed and characteristic "pencils" were selected from a large specimen of cylindrite and were finely ground to a homogeneous powder. Samples, each of which weighed about 100 to 200 mg, were sealed in polythene tubing. Standards were prepared from a dilute standard solution of Specpure indium (1 g per litre) in *M* nitric acid by weighing and sealing in a silica ampoule such an amount as would contain about the same weight of indium as in the amount of cylindrite taken, this being established from a preliminary experiment. Two standards and four samples were then packed into an aluminium can and irradiated simultaneously in the Harwell Pile for a period of 15 minutes only at a flux of about 10^{12} neutrons per sq. cm per second. After being left to "cool" for 2 days, the polythene tubes containing the samples were cut open and the material was brought into solution by being heated gently on a hot-plate with 5 ml of concentrated hydrochloric acid. After the bulk had dissolved, 1 ml of concentrated nitric acid was added and the digestion was continued. Apart from a small amount of free sulphur (which was shown to contain no indium activity) this treatment brought about complete solution of the sample. After the addition of a known weight of inactive indium as carrier, the chemical separation was carried out as previously described in detail[5] (steps 1 to 14), the radiochemically pure indium being finally precipitated and counted as the tris-oxinate. The chemical yield was determined gravimetrically after the conclusion of the counting. Typical results are shown in Table I.

Table I

Determination of indium in cylindrite by using indium-114

Sample No.	Nature	Weight, mg	Indium tris-oxinate formed, mg	Corrected* activity, counts per minute	Indium content, %
1	Cylindrite	170·2	17·5	4715	0·149
2	Cylindrite	161·2	21·5	4345	0·145
3	Cylindrite	149·1	22·2	3964	0·143
4	Cylindrite	140·0	16·4	3764	0·145
					0·146 ± 0·003
5	Indium standard	0·4249	35·0	7850	
6	Indium standard	0·4707	27·6	8760	

Standards—5: 7850 counts per minute per 0·4249 mg = 18,470 counts per minute per mg;
6: 8760 counts per minute per 0·4707 mg = 18,610 counts per minute per mg;
average: 18,540 counts per minute per mg of indium

* This column gives the counts per minute corrected for coincidences and background and corrected to 100 per cent. chemical yield, *i.e.*, 46·7 mg of indium tris-oxinate from the weight of carrier indium added.

Procedure for indium-116—

The determination of indium in cylindrite was carried out by the procedure previously described,[5] but samples and standards were irradiated for a period of 15 seconds only and processed as soon as possible. The radiochemical purity of the separated indium activity was confirmed, in every instance, by the measured half-life of 54·0 minutes. The results of these analyses are shown in Table II.

The chemical yield is generally about 50 per cent. It is perhaps noteworthy that even when, as a result of an accidental loss in sample A3, it was as low as 16 per cent., the result of the determination did not fall outside the range of values for all the samples, *i.e.*, 0·141 ± 0·005 per cent. of indium.

TABLE II

DETERMINATION OF INDIUM IN CYLINDRITE BY USING INDIUM-116

Sample No.*	Nature	Weight, mg	Indium tris-oxinate formed, mg	Corrected† activity, counts per minute	Indium content, %
A1	Cylindrite	122·2	20·9	5005	0·145
A2	Cylindrite	130·7	20·2	5480	0·149
A3	Cylindrite	146·0	7·6	5595	0·136
A4	Cylindrite	123·3	23·1	4875	0·140
					0·143 ± 0·006
A5	Indium standard	0·3983	36·1	11,040	
A6	Indium standard	0·3860	37·8	11,090	
	Standards—A5: 11,040 counts per minute per 0·3983 mg = 27,700 counts per minute per mg; A6: 11,090 counts per minute per 0·3860 mg = 28,700 counts per minute per mg; average: 28,200 counts per minute per mg of indium				
B1	Cylindrite	132·9	36·4	5700	0·136
B2	Cylindrite	115·1	35·5	5005	0·138
					0·137 ± 0·002
B3	Indium standard	0·2194	39·3	6840	
B4	Indium standard	0·2208	38·9	7020	
	Standards—B3: 31,200 counts per minute per mg; B4: 31,760 counts per minute per mg; average: 31,480 counts per minute per mg of indium				

* All samples with the same serial letter were irradiated simultaneously.

† This column gives the counts per minute corrected for coincidences and background and corrected for 100 per cent. chemical yield, based on 46·7 mg of indium oxinate for series A and 70·0 mg for series B.

PROCEDURE OF DIRECT COUNTING WITHOUT CHEMICAL SEPARATION—

In favourable cases it is possible to determine an element in the presence of several others by neutron activation without any subsequent chemical processing. For example, Boyd[6] has described the determination of about 1 per cent. of manganese and traces of sodium in an aluminium - manganese alloy, and Phillips and Cornish[7] found 12 per cent. of dysprosium in a sample of Specpure holmium oxide by a similar technique. The successful application of this method to a more complex mixture such as cylindrite will depend upon the ease and accuracy with which the composite decay curve for the irradiated sample can be resolved, for it is clearly essential that the activity due to the minor constituent, indium, being determined should not be masked by that due to any of the remaining elements.

Table III shows the nuclear characteristics of the isotopes of known constituents of cylindrite. When a nuclide formed on irradiation has a long half-life, of the order of days, the growth of its activity can be kept to negligible proportions by reducing the period of irradiation to about a minute or less: such cases are denoted by the letter *g* in the last column of Table III. When the half-life is short compared with that of indium-116, interference will be negligible if sufficient time is allowed for decay before starting to count; such isotopes are designated by the letter *d*. The calculated activity from the actual amounts of the various isotopes present in a 100-mg sample of cylindrite (assuming 0·15 per cent. of indium and the remaining composition as given above) after irradiation for 1 second at a flux of 10^{12} neutrons per sq. cm per second, followed by "cooling" for 30 minutes, is given in the last column of Table III.

The data show that 6 per cent. of the total activity after "cooling" for 30 minutes will be due to tin-121, tin-123, tin-125, antimony-122 and antimony-124, the contributions due to sulphur-37 and lead-209 being negligible. On further "cooling," the activity due to the 9·5-minute tin-125 and the 21-minute antimony-124 decays quite rapidly (see Table IV), and, although the half-life of tin-113 is much longer, it still decays faster than the indium. Moreover, owing to its low capture cross-section and lower natural abundance, interference from tin-113 never contributes more than 0·6 per cent. of the total activity. The most serious interference could arise from antimony-122, which makes a substantial contribution to the total activity from the very start. Since, further, it decays slowly with a half-life

of 2·8 days, after 9 hours' "cooling" when its activity has fallen by about 8 per cent. only, it is responsible for more than 99·9 per cent. of the total activity.

TABLE III

NUCLEAR CHARACTERISTICS OF ELEMENTS PRESENT IN CYLINDRITE

Target nuclide	Abundance, %	Isotopic activation cross-section, barns	Half-life	Activity per 100 mg of sample, d.p.m.
^{115}In	95·77	145	54·0 minutes	$9·44 \times 10^5$
^{32}S	0·017	0·14	5 minutes	21
^{122}Sb	57·2	5·7	3·5 minutes	*d*
			2·8 days	$3·3 \times 10^4$
^{124}Sb	42·6	0·03	21 minutes	$9·17 \times 10^3$
		0·03	1·3 minutes	*d*
		3·8	60 days	*g*
^{209}Pb	52	0·00045	3·3 hours	82
^{55}Fe	5·9	2·2	2·9 years	*g*
^{59}Fe	0·33	0·8	45 days	*g*
^{108}Ag	51·4	30	2·3 minutes	*d*
^{110}Ag	48·6	2	270 days	*g*
		82	24 seconds	*d*
^{113}Sn	0·95	1·3	112 days	*g*
^{117}Sn	14·2	0·006	14 days	*g*
^{119}Sn	24	0·01	250 days	*g*
^{121}Sn	33·0	0·001	71 years	*g*
		0·03	27 hours	530
^{123}Sn	4·7	0·001	130 days	*g*
		0·1	40 minutes	$5·9 \times 10^3$
^{125}Sn	6·0	0·2	9·5 minutes	$1·16 \times 10^4$
		0·004	10 days	*g*

d = interference is negligible if 30 minutes are allowed for decay before counting is started, as the half-life is short compared with that of indium-116.

g = interference is negligible if the time of irradiation is reduced to about a minute or less, as the half-life of the nuclide formed is long compared with that of indium-116.

TABLE IV

CALCULATED ACTIVITY FROM DIFFERENT ELEMENTS IN 100 mg OF CYLINDRITE AFTER IRRADIATION FOR 1 SECOND AND "COOLING" FOR VARIOUS TIMES

	"Time of cooling," hours						
Nuclide	½	1	2	3	4	6	9
^{116}In	94·40*	64·50	30·0	14·0	6·5	0·3	0·003
^{123}Sn	0·59	0·36	0·12	0·04	0·01	0	0
^{125}Sn	1·16	0·13	0·0	0·0	0	0	0
^{122}Sb	3·33	3·30	3·26	3·23	3·20	3·14	3·05
^{124}Sb	0·92	0·34	0·05	0·01	0	0	0
Percentage contribution of activity	94†	94	90	81	67	9·6	0·1
	97·3‡	98·7	99·5	99·8	100	100	100

* All activites are quoted in units of 10,000 disintegrations per minute.

† The figures in this horizontal row give the percentage contribution of activity from indium-116 to the total activity.

‡ The figures in this row give the percentage contribution of activity due to indium-116 to the total activity of all nuclides with the exception of antimony-112.

In the actual experiments, 100 mg of cylindrite weighed out accurately and sealed into polythene tubing were irradiated simultaneously with a dilute standard solution of indium for a short period, generally about 1 second, in the Harwell Pile at a flux of 10^{12} neutrons per sq. cm per second. The cylindrite was then removed from the polythene tubing, distributed uniformly over an aluminium counting tray and covered with Sellotape. The liquid standards, after the addition of 15 mg of indium carrier, were treated as before and the indium tris-oxinate was precipitated, mounted on an aluminium counting tray, dried and weighed.

Counting was started about 30 minutes after irradiation, the automatic counting assembly used registering the interval of counting, the count and the total accumulative time. Owing to the high activity of the irradiated cylindrite, the samples were placed on the lowest shelf in the lead castle and an aluminium absorber of about 80 mg of aluminium per sq. cm thickness was interposed between samples and the end-window counter. Counting, at 10 to 20-minute intervals, was continued for at least 12 hours, during which, without the mechanism of the counting assembly being stopped, points were obtained on the decay curve of the indium oxinate prepared from the standard. In any one determination the geometry and absorber thickness was kept constant, but in different determinations these were varied to suit the activity of the irradiated sample.

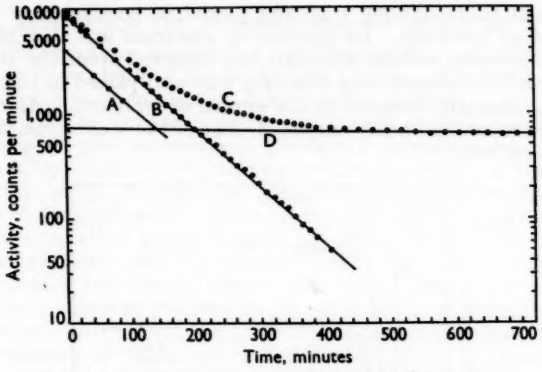

Fig. 1. Determination of indium in cylindrite by direct decay measurements: curve A, standard; curve B, resolved activity due to indium-116; curve C, measured activity; curve D, long-lived activity

A typical absorption curve is shown in Fig. 1. The activity due to indium alone is calculated by subtracting that due to nuclides of longer half-life.[6] The resulting slope, and that found for the irradiated standards, conforms exactly with the expected 54·0-minute half-life of indium-116. The activity of the standard (*d*) and the resolved activity (*c*) of the sample of cylindrite are read off at zero time, or at any other arbitrary time, and these values are used to compute the indium content of the sample, as shown in Table V.

TABLE V

DETERMINATION OF INDIUM IN CYLINDRITE BY DIRECT DECAY MEASUREMENTS

Experiment No.	Weight of sample (*a*), mg	Weight of standard (*b*), mg	Weight of indium oxinate, mg	Activity at zero time, counts per minute, for— sample (*c*)	standard (*d*)	standard (*e*)†	Indium found,‡ %
1	140·4	0·161	63·4	4220	3050	3404	0·14
2	101·4	0·211	62·5	3729	4300	4880	0·16

† Activity of the standard at zero time, corrected to 100 per cent. chemical yield, taking into account the amount of indium carrier, *viz.*, 70·8 mg of indium oxinate in experiment No. 1 and 71·0 mg in experiment No. 2.

‡ Calculated from the relationship: $\text{In, } \% = \frac{100\,bc}{ae}$.

DETERMINATION OF INDIUM BY DIRECT GAMMA-RAY SPECTROMETRY*—

Since the bulk of the gamma-ray activity produced on neutron irradiation of cylindrite will be due to the nuclear isomer indium-116*m* (half-life, 54·0 minutes), it should be possible to differentiate this activity from that due to other nuclides by means of a gamma-ray spectro-

* With L. Salmon.

meter; the actual concentration of indium should then be determinable without recourse to any chemical separation by comparison with a suitable standard.

The instrument used consisted of a 1-inch × 1½-inch thallium-activated sodium iodide crystal mounted on a 6260 E.M.I. photomultiplier tube. After suitable amplification, the output pulses from the photomultiplier were fed into a single-channel pulse-analyser and thence to a ratemeter. The output was fed into a recording potentiometer ganged to the bias sweep. In this way it was possible to obtain a gamma-ray spectrum as a plot of intensity (*i.e.*, counting rate, in arbitrary units) against gamma-energy.

Two small samples of cylindrite were sealed in polythene tubing and irradiated in the Harwell Pile for approximately 2 seconds, together with a dilute aqueous standard of indium (as nitrate) sealed in a silica ampoule. After irradiation, a sample was removed from its container, transferred to a counting tray and placed in position near the sodium iodide crystal in the counting assembly. Its gamma-ray spectrum was then plotted as described above. The dilute aqueous indium standard was removed from the silica ampoule after irradiation, evaporated to dryness on a counting tray and placed in the counting assembly in the exact position formerly occupied by the sample of cylindrite. After the measurement of its gamma-ray spectrum had been completed, that of the second sample of cylindrite was measured in the same way.

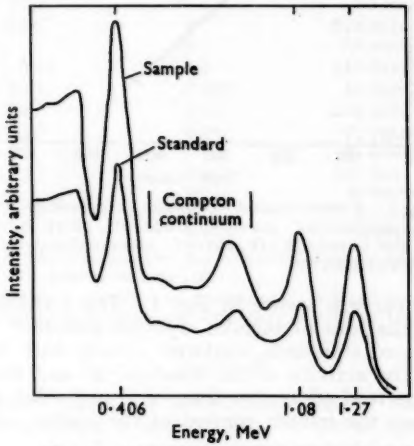

Fig. 2. Gamma-ray spectrogram of irradiated cylindrite

TABLE VI

DETERMINATION OF INDIUM IN CYLINDRITE BY GAMMA-RAY SPECTROMETRY

Nature	Sample weight, mg	Peak energy, MeV	Peak height, arbitrary units	Peak height corrected for decay, arbitrary units	Ratio of corrected peak heights for sample and standard	Indium found, %
Cylindrite	45·7	1·27	45·5	67	1·72	0·155
		1·08	50·5	74	1·68	0·151
		0·406	115	170	1·79	(0·161)
Cylindrite	47·2	1·27	31	68	1·74	0·152
		1·08	37	80	1·82	0·158
		0·406	79	175	1·84	(0·160)
Indium in standard solution	41·1	1·27	39	39		
		1·08	44	44		
		0·406	95	95		

As shown in Fig. 2, the characteristic spectrum of indium-116*m* given by the indium standard re-appears in the spectrum of the irradiated cylindrite. The heights of the three photo-peaks at 0·406, 1·08 and 1·27 MeV were measured in turn, and, after suitable corrections

had been made for decay during the plotting of the spectra, the concentrations of indium in cylindrite was calculated from the known weights of samples and indium standard, as shown in Table VI.

The ratio of the intensities of the gamma rays of 1·27 and 1·08 MeV is essentially the same in the cylindrite samples (1·10 and 1·17) as in the standard (1·13). However, the ratio of peak heights for 1·27 and 0·406 MeV is appreciably greater (2·54 and 2·57) for the samples than for the standard (2·43), which suggests that the 0·406-MeV peak in the cylindrite samples was enhanced by low-energy gamma activity other than that due to indium. When values for the indium content based on this low-energy peak are omitted, the average value of 0·15(4) per cent. of indium is obtained, in satisfactory agreement with the previous values.

Chemical Method for the Determination of Indium in Cylindrite

Facilities for radioactivation analysis are not common to every laboratory. But, since consistent values had been obtained for the indium content of cylindrite by four different methods, it seemed worth while to examine more familiar methods of analysis to see whether they would yield reliable results for a minor constituent of such a complex mineral.

There are no really selective volumetric or gravimetric procedures for indium. Absorptiometric determination by means of 8-hydroxyquinoline[8] or, better, 5:7-dichloro-8-hydroxyquinoline[9] is subject to many interferences, notably from lead, bismuth, tin, antimony and iron, many of which occur in cylindrite. Even greater difficulties attend the use of dithizone.[10] However, a procedure in which these reagents are used in succession would be feasible if most of the tin, lead and iron could be removed first. The low recoveries of indium from large samples of cylindrite reported by Brewer and Baker[4] (see p. 549 also) suggested that serious losses must occur through co-precipitation, and we have investigated these by using indium-114 as a tracer. In this way we have demonstrated that lead can be precipitated quantitatively by sulphuric or sulphamic acid, and that tin can be removed as its volatile bromide, there being no concommitant loss of indium in either procedure. Details will be published in a separate paper.[11] The efficiency of stages of solvent extraction into hydriodic acid (to effect a separation from iron)[12,13] and the completeness of the extraction of indium by dithizone were also followed radiometrically.

The full procedure finally adopted follows.

Reagents—

Ammonium citrate solution, 10 per cent.—Dissolve 84 g of the monohydrate in about 800 ml of distilled water, neutralise with ammonia solution, sp.gr. 0·880, to about pH 7, and make up to 1 litre.

Thymol blue indicator solution—Dissolve 0·1 g of the indicator in 0·1 *N* sodium hydroxide and make up to 100 ml.

Dithizone solution, 0·1 per cent.—Dissolve 0·5 g of analytical-reagent grade diphenylthiocarbazone (dithizone) in 500 ml of redistilled chloroform. Store the solution in the dark.

Sodium cyanide, 10 per cent.—Dissolve 100 g of analytical-reagent grade material in 1 litre of distilled water.

Potassium iodide solution—Dissolve 100 g of analytical-reagent grade material in water and make up to 100 ml.

Sodium metabisulphite solution, 1 per cent.—Prepare freshly as required by dissolving 1 g of the reagent in 100 ml of distilled water.

Acetate buffer solution—Dissolve 68 g of trihydrated sodium acetate in 250 ml of *M* acetic acid.

Oxine solution, 0·01 M—Dissolve 1·45 g of analytical-reagent grade 8-hydroxyquinoline in 1 litre of chloroform containing 1 per cent. v/v of ethanol.

Ammonia solution—Distil a concentrated solution or, preferably, pass ammonia gas from a cylinder into cold metal-free water until this is nearly saturated.

Impurities should be removed from the ammonium citrate, the sodium cyanide and the acetate buffer solution by extraction with successive portions of dithizone until the last extract remains green. Then remove any dissolved dithizone by repeated extractions with successive portions of chloroform.

The following acids are also required; these should be tested with dithizone for metallic impurities and, if necessary, made metal-free by repeated extraction.

Hydrochloric acid, sp.gr. 1·18.

Nitric acid, sp.gr. 1·42.
Perchloric acid, 72 *per cent.*
Hydrobromic acid, 46 *to* 48 *per cent.*
Sulphuric acid, sp.gr. 1·84.

PROCEDURE—

In the procedure that follows, the stages are numbered to facilitate reference in subsequent discussion—

(1) Weigh accurately about 100 mg of finely powdered cylindrite into a long-necked 100-ml round-bottomed flask fitted with a B19 socket. Add 2 ml of concentrated hydrochloric acid and heat to dissolve most of the mineral. Next add 1 ml of nitric acid, sp.gr. 1·42, 5 ml of 72 per cent. perchloric acid and 1 ml of sulphuric acid, sp.gr. 1·84, in that order, and continue heating until the sample is completely dissolved.

(2) Using apparatus with interchangeable cone and sockets of Pyrex glass, attach to the B19 socket of the flask a still-head carrying a 25-ml dropping funnel, a tube for introducing gases leading almost to the bottom of the round-bottomed flask and a side-arm connected to a water-cooled condenser and a receiver. Introduce dry nitrogen at the rate of about 6 bubbles a second. Heat the flask in a bath of sulphuric acid to 230° C and volatilise tin and antimony by introducing 10 ml of 46 to 48 per cent. hydrobromic acid dropwise from the funnel over a period of about 30 minutes.

(3) Remove the heating bath, stop the flow of nitrogen, and allow the apparatus to cool. Dismantle those parts of the apparatus attached to the distilling flask and wash into it any liquid adhering to the nitrogen inlet-tube. Evaporate the contents of the flask until copious fumes of perchloric acid are produced. Continue heating to remove almost all the perchloric acid, at which point there is an easily detectable and sudden decrease in the amount of fumes produced while the rate of heating is maintained steadily. The volume at this stage should be about 1 ml.

(4) Allow the flask to cool and rinse down the sides with about 10 ml of distilled water. Mix the contents thoroughly and transfer them to a 50-ml centrifuge tube, rinsing the sides of the flask with several small successive portions of water. Spin in a centrifuge, and transfer the supernatant liquid to a 125-ml Erlenmeyer flask. Wash the precipitate of lead sulphate with three 10 to 15-ml portions of water, spinning in the centrifuge each time and combining the supernatant liquids in the Erlenmeyer flask.

(5) Evaporate the combined supernatant liquids and washings on a hot-plate to between 10 and 15 ml. Cool the solution to room temperature and transfer it quantitatively to a 100-ml separating funnel; dilute the solution and washings to a final volume of 25 ml. Add 2 ml of ammonium citrate solution and three drops of thymol blue indicator solution, and neutralise with ammonia solution until the indicator just turns yellow. Add 5 ml of dilute perchloric acid (1 + 9) and extract successively with two 5-ml portions of dithizone solution. If the second extract is not a clear green, repeat for a third or fourth time. Extract once with 5 ml of chloroform. Discard all organic phases.

(6) To the aqueous phase add three drops of thymol blue indicator solution and add ammonia solution until the indicator just turns purple (pH 9·0 to 9·3). Add 5 ml of sodium cyanide solution and extract the indium with three 10-ml portions of dithizone solution and once with 5 ml of pure chloroform. The last two extracts should have a pure green colour. Discard the aqueous phase.

(7) Collect all the chloroform extracts in a second separating funnel and shake them with four 5-ml portions of 2 *N* sulphuric acid. Combine these acid extracts (using 5 ml of rinsing water) and extract once with 5 ml of chloroform to remove excess of dithizone. Reject the organic phases.

(8) Add 5 ml of potassium iodide solution and extract the indium with three 10-ml portions of diethyl ether. Remove the indium from the ethereal extracts with four 5-ml portions of 0·1 *M* hydrochloric acid.

(9) Collect the combined acid extracts in a 100-ml separating funnel and add 1 ml of sodium metabisulphite solution. Remove any colouring matter left in this solution by extracting with 5-ml portions of chloroform until a completely colourless extract is obtained. Reject the organic layers.

(10) Add 5 ml of acetate buffer solution and extract with four 5-ml portions of oxine solution. Collect these extracts in a 25-ml calibrated flask and dilute to the mark with pure chloroform. Measure the optical density of an aliquot portion at 400 mμ.

Calculate the indium content with reference to a standard curve prepared by adding x ml of a standard indium solution in 0·1 *M* hydrochloric acid to (20 − x) ml of 0·1 *M* hydrochloric acid and carrying this through stages (9) and (10).

Discussion

The absorptiometric determination of indium by extracting its oxine complex at pH 3·5 is said by Moeller[8] to be possible in the presence of Mg, Ca, Sr, Cd, Hg, Sn^{IV}, Pb, Mn, Cr^{III} and Ag, but more or less interference can be expected from Al, Ga, Tl^{III}, Sn^{II}, Bi, Cu^{II}, Fe^{II}, Fe^{III}, Ni and Co. Gentry and Sherrington[14] described the absorptiometric determination of tin by extracting tin^{IV} into a chloroform solution of oxine at pH 3·5. Teicher and Gordon[15] could not repeat this work, but our own measurements show that tin is at least partly extracted under these conditions. However, $antimony^{III}$ was not found to be extracted at pH 3·5 by the oxine reagent.

Preliminary experiments showed that the stage of volatilisation as bromides reduced interference from tin and antimony, and that lead could be precipitated quantitatively as the sulphate. Interference from iron was reduced by the solvent-extraction procedures[12,13] incorporated in stage (8). The final stages in the above procedure follow the suggestions of May and Hoffman,[10] which have recently been elaborated by Luke and Campbell[16] in a procedure for the determination of microgram amounts of indium in germanium. Their procedure needed considerable modification for the present purpose in view of the much greater concentrations of iron and other interfering elements. Luke and Campbell observed that when indium was reverted into dilute acid from a dithizone extract in chloroform it was accompanied by coloured organic material, which introduced errors into the subsequent absorptiometric determination of indium as its oxine complex. To overcome this they destroyed all the dithizone and coloured organic impurities by wet-oxidation with perchloric acid. This tedious stage has been replaced in our procedure by the quicker and equally effective process of solvent extraction (stage (9)) immediately before the addition of oxine.

Results

Figures for the indium content of the sample of cylindrite previously analysed radiometrically at Harwell are shown in Table VII. They are in excellent agreement with the determinations summarised in Tables I, II, V and VI. Table VII also includes values for a different sample of cylindrite that proved to be richer in indium.

Table VII

Absorptiometric determination of indium in cylindrite

	Weight taken, mg	Optical density of oxinate solution	Weight of indium, mg	Indium found, %
Sample previously analysed radiometrically	102·1	0·345	152	0·149
	103·5	0·340	150	0·145
	112·0	0·370	163	0·146
New large sample of cylindrite	106·5	0·501	225	0·212
	106·0	0·496	223	0·210
	102·6	0·492	221	0·215

Experience with all the methods described above leaves no doubt that the use of radiometric methods after neutron activation are the more convenient and reliable. The absorptiometric method demands a quantitative transfer of indium at each of a large number of stages; failure to remove completely certain interfering elements will increase the final optical density of the oxine extract and lead to spurious high values for indium. On the other hand, quite apart from its greater sensitivity, a procedure based on neutron-activation analysis with use of indium-114 or indium-116 does not require such a consistently high degree of experimental skill, adventitious losses of indium being compensated for by the correction based on the chemical yield. There is no uncertainty about the composition of the final determination form, for the radiochemical purity of the material finally counted can be assessed by a variety of sensitive and specific means, such as the measurement of the characterising half-life of

the nuclide formed and a study of its energy spectrum.[5] Further, the presence of trace amounts of indium in any or all of the reagents used in the chemical processing is without influence on the final result.

We have also explored the possibility of analysing cylindrite (or similar indium-rich minerals) by adding to a sample a known weight of indium-114 of high specific activity. Measurement of the activity of the indium finally isolated as the oxine complex by the procedure detailed on pp. 556 and 557 then provides the necessary results for correcting the total weight of indium in the system (as determined absorptiometrically) for adventitious losses during the chemical separations.

We are grateful to Mr. F. M. Brewer for supplying the samples of cylindrite; and to Mr. A. A. Smales for his constant encouragement and advice, and for the generous provision of laboratory facilities. One of us (J. van R. S.) is indebted to the Rhodes Trustees for the award of a Scholarship.

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Photometric Determination of Molybdenum in Tungsten Ores

By P. G. Jeffery

The suppression by citric acid of the formation and subsequent extraction of the complex of tungsten with toluene-3:4-dithiol is used to permit the determination of molybdenum to be made in tungsten ores. Complete suppression does not occur, and, when the concentration of molybdenum is less than 500 p.p.m., measurement of the optical density of the organic extract at two wavelengths must be made to correct for the tungsten extracted with the molybdenum as complex with the reagent.

Ores of the two tungsten-producing areas of the Uganda Protectorate have been characterised by King[1] on the basis of their manganese contents. A recent investigation has shown that this difference in manganese is parallelled by a similar difference in the molybdenum contents of ore samples from the two areas. The ferberite and reinite ores of Kigezi contain less than 50 p.p.m. of molybdenum trioxide, whereas the wolframite deposits associated with the Singo Batholith contain 0·1 to 0·3 per cent.

The possibility of determining the molybdenum in these ores, in the presence of tungsten, as the complex with toluene-3:4-dithiol was suggested by the work of Bickford, Jones and

Keene,[2] who used a 2 per cent. citric acid solution at a pH of 1·8 to suppress the formation of the tungsten complex with this reagent. These workers noted that complete suppression of the tungsten complex with toluene-3:4-dithiol did not occur and that, under the conditions described by them, an average of 99·74 per cent. of the total tungsten present was not precipitated. In order to determine molybdenum contents of only a few parts per million in tungsten ores, it is necessary to retain 99·99 per cent. or more of the tungsten in solution. This is not possible in sulphuric - citric acid or hydrochloric - citric acid solutions and, in my experience, the required degree of suppression can only be obtained in phosphoric - citric acid solutions.

Examination has shown that in such solutions molybdenum can be completely precipitated as the complex with toluene-3:4-dithiol, which can then be extracted with light petroleum. The optical density of the extract is, however, a function of the acid concentration. With phosphoric acid at a concentration of 8 per cent. v/v, the optical density of the extract corresponds to that of similar extracts from sulphuric and hydrochloric acid solutions containing the same amount (20 per cent. w/v) of citric acid (see Fig. 1, p. 561), and also to that of similar extracts from sulphuric acid solutions obtained under the conditions described by Allen and Hamilton,[3] that is, in the absence of citric acid. Under the conditions described below, a few micrograms of tungsten are also extracted as reagent complex into the organic solution. By using the method of measurement of optical density at two wavelengths as previously described,[4] the molybdenum concentration is readily determined from the equations—

$$D_{630\,m\mu} = a\,[MoO_3] + b\,[WO_3]$$
$$D_{680\,m\mu} = a'[MoO_3] + b'[WO_3]$$

where the values of the constants a and b at 630 mμ and 680 mμ are determined experimentally as described below. When the molybdenum content of the ore sample exceeds 500 p.p.m., the tungsten extracted with the molybdenum as the complex with toluene-3:4-dithiol may be neglected and the determination completed by measurement of the optical density of the extract at a wavelength of 680 mμ.

The values of the constants a and a' in the above equations can be determined by applying the procedure described to known amounts of standard molybdenum solution. The constants b and b' cannot be obtained by a similar procedure, as only a small and unknown proportion of the tungsten is extracted. This difficulty may be overcome in the following way. Rearranging the equations—

$$D_{630\,m\mu} - a\,[MoO_3] = b\,[WO_3] \text{ and}$$
$$D_{680\,m\mu} - a'[MoO_3] = b'[WO_3], \text{ hence}$$
$$\frac{b}{b'} = \frac{D_{630\,m\mu} - a\,[MoO_3]}{D_{680\,m\mu} - a'[MoO_3]}.$$

By applying the procedure described to "molybdenum-free" tungsten solutions the ratio b/b' may readily be determined without a knowledge of the proportion of the tungsten extracted. From this ratio and the constants a and a', the molybdenum content of any given sample can be found by means of the above equation.

"Molybdenum-free" tungsten is not however generally available, and the tungsten compounds that are available contain too much molybdenum for this procedure, which is very sensitive to molybdenum content, to be applied.

An alternative procedure for the evaluation of the ratio b/b' is based on the observation that by increasing the temperature of the solution the proportion of tungsten extracted as complex with toluene-3:4-dithiol is increased. Since temperature changes do not affect the quantitative nature of the molybdenum extraction, the optical densities of two extracts prepared from similar tungsten solutions under the conditions described, but at temperatures t_1 and t_2, are given by—

$$D^{t_1}_{630\,m\mu} = a[MoO_3] + b[WO_3^{t_1}] \text{ and}$$
$$D^{t_2}_{630\,m\mu} = a[MoO_3] + b[WO_3^{t_2}], \text{ hence}$$
$$(D^{t_1} - D^{t_2})_{630\,m\mu} = b(WO_3^{t_1} - WO_3^{t_2}).$$

A similar equation in b' is obtained at 680 mμ, from which the ratio b/b' can be calculated.

A less complicated procedure that I have adopted to determine the constants b and b' is to put known amounts of pure tungsten solutions through the procedure previously described,[4] that is, in the absence of citric acid and at the correct acid concentration for quantitative extraction of tungsten. The values of b and b' determined under these conditions are applicable under the conditions described below, since the effect of the citric acid is to inhibit to a large extent the formation of the tungsten - toluene-3:4-dithiol complex, but once this complex is formed, then precipitation and subsequent extraction follow whether or not citric acid is present. The optical density of the extract is given by $\log I_0/I = b[WO_3]$, where $[WO_3]$ is the concentration of tungsten in the complex and b is the constant as determined in the absence of citric acid. This is only true if the mutual solubilities of light petroleum and the aqueous phase remain the same. That they do so is shown by the observation that the optical densities of extracts from molybdenum solutions are not affected by the presence of citric acid in the aqueous phase.

The sample is decomposed by fusion with sodium hydroxide in the usual way. The aqueous solution of the melt is filtered free of oxides of iron and manganese, and diluted to a known volume. To an aliquot of this solution containing up to 40 μg of molybdenum trioxide are added citric acid, a small amount of iron to intensify the colour of the complex, as described by Allen and Hamilton,[3] and phosphoric acid. The complex of molybdenum with toluene-3:4-dithiol is then precipitated by adding the dithiol reagent and allowing the solution to stand for 1 hour at room temperature. Close control of the temperature is not necessary, and in the range 15° to 25° C the formation of the tungsten complex with toluene-3:4-dithiol is restricted to a small and reasonably constant degree. A known volume of light petroleum is added and the precipitated complexes of tungsten and molybdenum are extracted into the organic phase.

Of the elements normally occurring in tungsten ores that accompany the molybdenum into the filtrate from the alkaline fusion, only tin interferes with the determination. The presence of tin in the solution is indicated by the gradual appearance of a red colour in the solution after the addition of the dithiol reagent. This red complex of tin is insoluble in light petroleum, but collects at the boundary between the two phases and is easily removed by filtration of the separated organic solvent through an open-textured filter-paper. In the presence of much tin it would be necessary to add an increased amount of the dithiol reagent.

Experimental

In Fig. 1 is shown the extent to which the optical density of the organic extract is dependent upon the acid concentration of the aqueous phase. In a 20 per cent. w/v citric acid solution, concentrations of approximately 8 per cent. v/v of hydrochloric, sulphuric or phosphoric acid result in uniform precipitation and extraction of the molybdenum complex. The optical densities of extracts obtained from molybdenum solutions under these conditions are identical with the optical densities of extracts obtained from similar molybdenum solutions under the conditions for complete precipitation and extraction of the molybdenum complex described by Allen and Hamilton,[3] that is, in the absence of citric acid.

The suppression of the tungsten complex with toluene-3:4-dithiol in sulphuric - citric acid and in phosphoric - citric acid solutions is shown in Table I. In these experiments a citric acid concentration of 2 per cent. w/v, as described by Bickford *et al.*,[2] was used.

Table I

Suppression of tungsten - dithiol complex

Acid concentration	Tungsten trioxide taken, mg	Tungsten trioxide recovered, μg
5% v/v of sulphuric acid	100	108
20% v/v of sulphuric acid	100	103
5% v/v of phosphoric acid	80	5

The extraction of tungsten from phosphoric - citric acid solutions, determined as described, by measurement of the optical density at 630 mμ and at 680 mμ, is shown in Fig. 2. By increasing the concentration of citric acid in the aqueous phase, increased suppression of the tungsten complex was obtained. High concentrations of citric acid have

the effect of increasing the sensitivity of the procedure to variation in the phosphoric acid concentration and so for this reason a concentration of citric acid greater than 20 per cent. is not desirable.

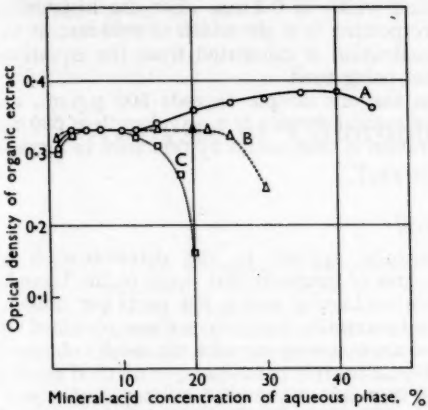

Fig. 1. Relation between mineral-acid concentration of the aqueous phase and the optical density of the light petroleum extract: curve A, phosphoric acid; curve B, sulphuric acid; curve C, hydrochloric acid. The concentration of citric acid in the aqueous phase was 20 per cent.

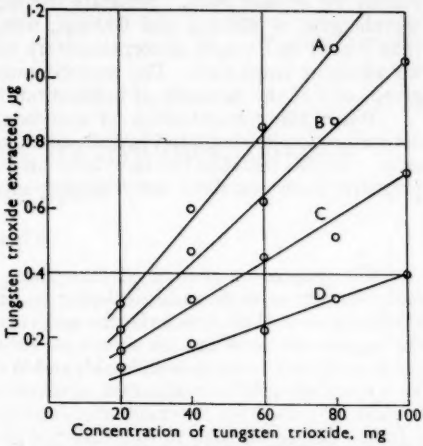

Fig. 2. Relation between tungsten extracted and tungsten present in citric - phosphoric acid solution: curve A, 20 per cent.; curve B, 30 per cent.; curve C, 40 per cent.; and curve D, 50 per cent. of citric acid

Method

Reagents—

Toluene-3:4-dithiol solution—Dissolve 1 g of the reagent in 300 ml of a 1 per cent. aqueous sodium hydroxide solution. When solution is complete, add 5 ml of thioglycollic acid. Store this solution in a refrigerator.

Iron solution—Dissolve 1 g of pure iron wire in 20 ml of diluted sulphuric acid (1 + 1 v/v) and dilute to 1 litre.

Light petroleum—The product X3B, supplied by the Shell Company of East Africa, with a nominal boiling point range of 100° to 132° C, was used. Purify the solvent before use by shaking with concentrated sulphuric acid, neutralising and washing with water.

Phosphoric acid—Analytical-reagent grade was used, containing approximately 90 per cent. of H_3PO_4 by weight.

Citric acid solution, 100 per cent. w/v—Purify this solution by shaking it with a small amount of a cation-exchange resin. Zeo-Karb 225 resin was found to be suitable for this purpose.

Standard molybdenum solution—Dissolve 0·25 g of pure molybdenum oxide in a small amount of ammonium hydroxide, and dilute to 250 ml with water. From this solution, prepare a working solution containing 10 µg per ml by dilution with water when required.

Standard tungsten solution—Prepare the tungsten solution similarly, using 0·25 g of pure tungstic oxide.

Procedure—

Fuse a 1-g sample of the finely powdered tungsten ore with 8 g of sodium hydroxide in an iron or nickel crucible. When the fusion is complete, extract the cold melt with water containing a few drops of ethanol. Collect the residue on a hardened filter-paper, and wash the precipitate well with a hot 2 per cent. sodium carbonate solution. Discard this residue and dilute the filtrate to 250 ml in a calibrated flask.

By pipette put an aliquot of this solution, containing not more than 40 µg of molybdenum trioxide, into a stoppered flask of approximate capacity 100 ml. Add 10 ml of the citric acid solution, 1 ml of the iron solution and sufficient phosphoric acid to neutralise the sodium hydroxide in the aliquot and to provide approximately 5 ml in excess. Dilute the solution

to 50 ml, and add 5 ml of toluene-3:4-dithiol solution. After setting the solution aside for 1 hour at room temperature, add exactly 10 ml of light petroleum and extract the molybdenum complex into the organic phase by shaking for three separate periods of approximately 90 seconds each. Separate the organic phase, and determine the optical density at wavelengths of 630 mμ and 680 mμ, using a band width of 0·3 mμ. For the instrument that I used (a Uvispek absorptiometer) this corresponded to a slit width of 0·06 mm at the wavelengths employed. The molybdenum concentration is calculated from the equations given, one of the methods of calibration described being used.

When the concentration of molybdenum in the ore sample exceeds 500 p.p.m., the determination is completed by measurement of the optical density at a wavelength of 680 mμ only. In this instance the molybdenum concentration is then found by reference to a graph prepared from standard molybdenum solutions.

Discussion

The procedure described has been successfully applied to the determination of molybdenum in wolframite, ferberite and reinite, ores of tungsten that occur in the Uganda Protectorate. With the ferberite and reinite ores, containing only a few parts per million, the results obtained are, as shown in Table II, substantially lower than those obtained by the thiocyanate method of Grimaldi and Wells,[5] but are in agreement with the results obtained by a spectrographic examination in which a semi-quantitative cathode-layer method similar to that described by Mitchell[6] was employed. A step sector was used in conjunction with a Judd - Lewis comparator to enable the molybdenum content of ore samples to be compared with that of standard samples. These samples were prepared by grinding pure tungstic oxide with a ferberite sample in which molybdenum could only just be detected by the cathode-layer procedure.

Table II

Determination of molybdenum in ores by various methods

Sample No.	Molybdenum trioxide found by the method of Grimaldi and Wells, p.p.m.	Molybdenum trioxide found by the proposed method, p.p.m.	Molybdenum trioxide found by a spectrographic method, p.p.m.
18,405	45	10	10 ± 5
18,406	65	12	10 ± 5
18,407	60	9	10 ± 5

In the determination of the minimum sensitivity of molybdenum in an iron tungstate base by the spectrographic method, a similar difficulty arises to that described above, namely that "molybdenum-free" tungsten is not generally available. Comparison of spectrograms taken by using the stepped sector of samples of the ferberite base containing a few parts per million of added molybdenum with similar spectrograms of the base indicated that the molybdenum content of the base was in the range 4 to 7 p.p.m. The results given in Table II are based on this figure and on the limiting accuracy of determinations of this type, given by Mitchell[7] as ±30 per cent. of the amount present.

In order to test the method for completeness of recovery of molybdenum from the acid solution, aliquots of standard molybdenum solution were added to aqueous phosphoric - citric acid solutions of the ore (sample No. 18,407, ferberite from Kigezi) and the determinations were completed as described. The results were as follows—

Molybdenum trioxide added, μg	.. ..	—	5·0	10·0	15·0
Molybdenum trioxide found, μg	.. ..	0·9	5·8	10·9	15·8

I am grateful to the Director, Geological Survey of Uganda, for permission to publish this paper.

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Analysis of Chlorophenols by Anion-exchange Chromatography

BY D. LOGIE

An ion-exchange chromatographic method is described that has been successfully applied to the analysis of commercial 2:4:5-trichlorophenol and 2:4-dichlorophenol samples. The method involves the use of the acetate salt of the strongly basic anion-exchange resin De-Acidite FF in a non-aqueous solvent medium of pure methanol. The separation of the phenols is achieved either by graded elution with glacial acetic acid - methanol mixtures or by controlled pH of the eluting medium by using triethylamine - acetic acid buffer solutions in methanol. Ultra-violet absorption measurements are employed for the detection and determination of the separated phenols. The technique should be of general application to the separation and analysis of phenolic compounds.

Part I. Determination of 2:4:5- Isomer in Commercial 2:4:5-Trichlorophenol

THIS work was undertaken in an attempt to resolve the difficulties encountered in the analysis of the higher chlorinated phenols, which are of importance in the preparation of selective weedkillers and in the dye-stuffs industry.

A considerable amount of preliminary work was carried out on crude 2:4:5-trichlorophenol by fractional precipitation methods. By careful addition of controlled amounts of dilute hydrochloric acid to an aqueous solution of the sodium salt of the crude material, many fractions were obtained. The least acidic fraction was shown to contain an increased proportion of a "methoxy" compound, and the most acidic fraction contained about 30 per cent. of an impurity that, from its infra-red absorption spectrum, was identified as the 2:3:6- isomer. When pure specimens of the 2:3:6- and 2:4:5- isomers became available, an infra-red absorption method was developed for the determination of these two components. The total analysis, however, remained 10 to 15 per cent. short of 100 per cent. and the infra-red method failed to indicate or identify any other impurities. In view of this fact and the requirement of a method that would be adaptable to routine analysis in control laboratories, the investigation was continued.

Since appreciable separation of some of the impurities in the crude material had been achieved by fractional precipitation with acid, the possibility of applying ion-exchange methods to this problem was considered. It was known from the literature that the strongly basic anion-exchange resins in the free-base form would absorb weak acids such as boric acid or phenol.[1] No information was available, however, about the desorption of phenol from these resins.

As the trichlorophenols are sparingly soluble in water, the use of aqueous solutions of their sodium salts was first examined. It was found possible to absorb the trichlorophenols quantitatively from such solutions on a strongly basic anion-exchange resin in the free-base form, *e.g.*, Amberlite IRA-400 (OH) or De-Acidite FF (OH). Subsequent attempts to desorb the phenols with aqueous sodium hydroxide were unsuccessful even when concentrations up to 5 *N* were employed.

The elution of the phenols, absorbed on the free-base resin, with aqueous hydrochloric acid was impossible owing to the precipitation of the free phenols in the column. The use of 50 per cent. ethanol as a solvent medium, however, retained the phenols in solution and rapid elutions were possible. These conditions gave rise to a "displacement analysis" type of

chromatogram, but the phenols "tailed" out considerably and so effectively prevented further development of this technique.

The solvent medium was changed to pure methanol to avoid any solubility effects, and other forms of the resin were sought that would permit acidic conditions to be employed for the elutions. It was finally found possible to absorb the free 2:4:5-trichlorophenol in methanol solution on the acetate form of the resin. The subsequent elution of the phenol could easily be achieved with methanol solutions of glacial acetic acid. As the solvent and eluting agents were aliphatic, ultra-violet absorption was adopted for the detection and determination of the eluted phenols.

Experimental

Behaviour of 2:4:5-trichlorophenol on a micro-resin column—

The original experiments were carried out on a micro-column, 8·5 mm × 30 mm, of 100 to 200-mesh B.S.S. Amberlite IRA-400 (acetate form), with methanol as solvent and a rate of flow of approximately 1 ml per minute. A loading of 10 mg of 2:4:5-trichlorophenol in 2 ml of methanol was transferred to the column, and the column was eluted with 50 ml of methanol. Ultra-violet absorption measurements on the effluent showed that the absorption was quantitative.

The column was then eluted with a 1 per cent. v/v solution of acetic acid in methanol, and the effluent was collected in 10-ml fractions and their absorptions were measured at 292 mμ (the peak wavelength, see Fig. 7, p. 567) in 1-cm cells. The 2:4:5-trichlorophenol was rapidly eluted, as shown by the following results—

Fraction No.	1	2	3	4	5	6
Absorption	1·65	1·57	1·02	0·31	0·06	0·01

Behaviour of trichlorophenol isomers on a large column—

A larger column, 16 mm × 225 mm, of 100 to 200-mesh B.S.S. Amberlite IRA-400 (acetate form) was prepared, with methanol as solvent, and a rate of flow of 1·5 ml per sq. cm per minute was adopted.

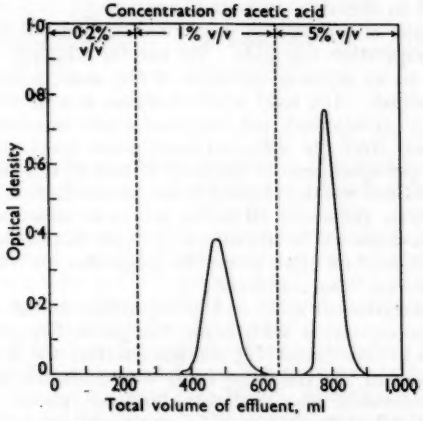

Fig. 1. Separation of 2:4:5- and 2:3:6-trichlorophenol on a 16-mm × 250-mm column of 100 to 200-mesh B.S.S. De-Acidite FF (acetate form); solvent, methanol; rate of flow, 1·5 ml per sq. cm per minute. Loading of column, 5 mg of 2:4:5- isomer and 5 mg of 2:3:6- isomer. The optical densities were measured at 280 mμ in 1-cm cells

A loading of 5 mg each of the 2:4:5- and 2:3:6- isomers was transferred to the column and an intial elution was attempted with a 0·2 per cent. v/v solution of acetic acid in methanol. No phenols were eluted in 470 ml of effluent.

The elution was continued with 400 ml of a 1 per cent. v/v solution of acetic acid in methanol, and the effluent was collected in 10-ml fractions and their absorptions were measured at 292 mμ in 1-cm cells. A symmetrical elution peak was obtained, similar to that shown in Fig. 1, which was obtained with De-Acidite FF under similar conditions (see later).

It was noted, however, from total absorption measurements, that the amount of phenol in this peak was only about 5 mg. This indicated that a separation of the phenols had occurred and was confirmed by continuing the elution with a 5 per cent. v/v solution of acetic acid in methanol. A second symmetrical elution peak was obtained, as shown in Fig. 1.

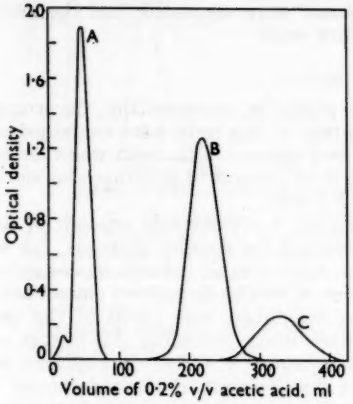

Fig. 2. Elution of other phenols from a 16-mm × 250-mm column of 100 to 200-mesh B.S.S. De-Acidite FF (acetate form); solvent, methanol; rate of flow, 1·5 ml per sq. cm per minute. Loading of column: curve A, 5 mg of 2:4-dichloro-5-methoxyphenol; curve B, 5 mg of 2:4-dichlorophenol; curve C, 2 mg of 3:4:5-trichlorophenol. The optical densities were measured at 290 mμ in 1-cm cells

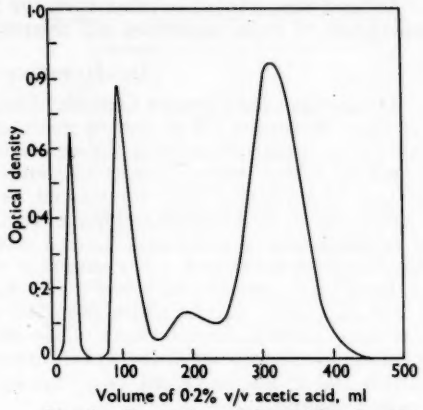

Fig. 3. Separation of impurities in commercial 2:4:5-trichlorophenol on a 16-mm × 250-mm column of 100 to 200-mesh B.S.S. De-Acidite FF (acetate form); solvent, methanol; rate of flow, 1·5 ml per sq. cm per minute. Loading of column: 100 mg of crude 2:4:5-trichlorophenol. The optical densities were measured at 290 mμ in 1-cm cells

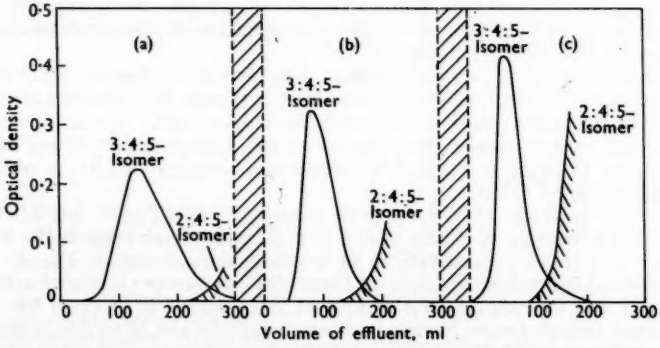

Fig. 4. Separation of 2:4:5- and 3:4:5-trichlorophenol on a 13-mm × 30-mm column of 100 to 200-mesh B.S.S. De-Acidite FF (acetate form); solvent, methanol; rate of flow, 3 ml per minute. Loading of column: 2 mg of 3:4:5- isomer and 20 mg of 2:4:5- isomer. Elution with (*a*) 0·015 per cent. v/v; (*b*) 0·020 per cent. v/v; (*c*) 0·030 per cent. v/v acetic acid. The optical densities were measured at 290 mμ in 1-cm cells

An examination of the ultra-violet absorption spectra of fractions from each peak showed that the material eluted by the 1 per cent. v/v solution of acetic acid in methanol was pure

2:4:5-trichlorophenol, whereas that from the 5 per cent. v/v solvent was pure 2:3:6-trichlorophenol.

A further study of several possible impurities, *viz.*, 2:4-dichlorophenol, 3:4:5-trichlorophenol and 2:4-dichloro-5-methoxyphenol, was undertaken, and the elutions of these phenols from the same column is as shown in Fig. 2. All these compounds were eluted with a 0·2 per cent. v/v solution of acetic acid in methanol.

As the separation of the trichlorophenol isomers was so great, the loading of the column was increased. A typical graded elution of the impurities from 100 mg of crude 2:4:5-trichlorophenol is as shown in Fig. 3.

At least four impurities other than the 2:3:6- isomer were separated, and the further examination of these impurities was reserved for future work.

Development of the method

At this stage the Permutit Company Limited made available, commercially, the strongly basic resin De-Acidite FF in various mesh sizes. Samples of this resin were examined and found to be equally effective in the separations described above. This resin was therefore adopted for further work, in order to eliminate the tedious process of grinding and sieving that had been required with commercial Amberlite IRA-400.

With the graded-elution technique with large columns, a considerable amount of time was required, and in order to achieve a more rapid method for routine purposes, the size of the column was reduced. The elution of the phenols from a small column was examined with lower concentrations of acetic acid. In connection with the impurities eluted before the 2:4:5- isomer, in the above-described procedure, advantage was taken of the close similarity in elution characteristics of the impurity immediately preceding this isomer and the elution characteristics of the 3:4:5- isomer. A specimen of 3:4:5-trichlorophenol was available and it was employed as a "marker" for the development of the separations on the small column.

Behaviour of the trichlorophenol isomers on a small column—

A small column, 13 mm × 30 mm, of 100 to 200-mesh B.S.S. De-Acidite FF (acetate form) was prepared, with methanol as solvent, and a rate of flow of 3 ml per minute was adopted.

(*a*) *Concentration of sample solution*—It was found by experiment that the 3:4:5-isomer could be eluted from this column with a 0·02 per cent. v/v solution of acetic acid in methanol. The absorption of the phenol on the resin releases (as in normal ion-exchange reactions) the equivalent amount of acetic acid. In order, therefore, to preserve uniform conditions during absorption and elution, the phenol samples were prepared at a concentration of 1 mg per ml (0·1 per cent. w/v); this concentration of phenol released about 0·02 per cent. v/v of acetic acid in the effluent.

(*b*) *Maximum loading of a small column*—The maximum loading of 2:4:5-trichlorophenol that could be handled safely on this size of column was determined by running a 0·1 per cent. w/v solution in methanol through the column until "break-through" occurred. The break-through capacity under these conditions was approximately 35 mg per ml of resin. A standard loading of 20 mg of the 2:4:5- isomer was adopted for further work, to provide a considerable margin of safety.

(*c*) *Effect of the mesh size of the resin on the separation of the* 2:4:5- *and* 3:4:5- *isomers*—The separation of a mixture of 20 mg of the 2:4:5- isomer and 2 mg of the 3:4:5- isomer on the column at various concentrations of acetic acid is shown in Fig. 4.

Some cross-contamination occurs in all these elutions and the effect of utilising resin of a finer mesh size was investigated. A sample of De-Acidite FF supplied by the Permutit Company Limited and quoted as having an average particle size of 50 μ was used to prepare a new column with identical dimensions, *viz.*, 13 mm × 30 mm. All other conditions were as before and the same phenol mixture was examined. A complete separation of the isomers was achieved, as shown in Fig. 5.

(*d*) *Separation of the* 2:4:5- *and* 2:3:6- *isomers*—By means of further experiments in which this 50-μ resin column was used, a complete separation of the 2:4:5- and 2:3:6-isomers was obtained, the separation being achieved by continuing the elution with the acetic acid at concentrations of 0·2 per cent. v/v and 5 per cent. v/v. A typical separation of 20 mg of the 2:4:5- isomer and 1 mg of the 2:3:6- isomer is shown in Fig. 6.

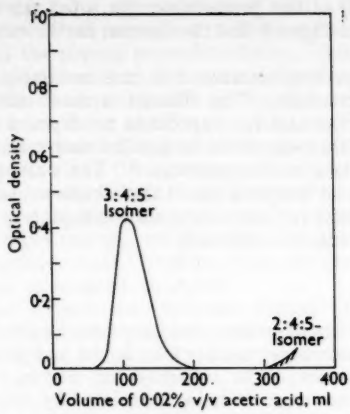

Fig. 5. Separation of 2:4:5- and 3:4:5-trichlorophenol on a 13-mm × 30-mm column of "50-μ" De-Acidite FF; solvent, methanol; rate of flow, 3 ml per minute. Loading of column, 2 mg of 3:4:5- isomer and 20 mg of 2:4:5- isomer. The optical densities were measured at 290 mμ in 1-cm cells

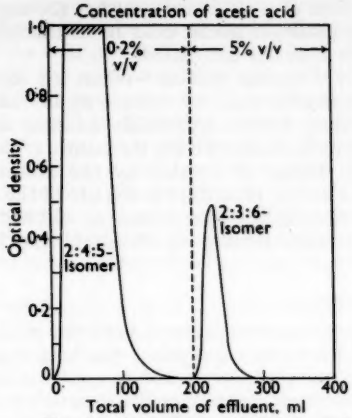

Fig 6. Separation of 2:4:5- and 2:3:6-trichlorophenol on a 13-mm × 30-mm column of "50-μ" De-Acidite FF (acetate form); solvent, methanol; rate of flow, 3 ml per minute. Loading of column, 20 mg of 2:4:5- isomer and 1 mg of 2:3:6- isomer. The optical densities were measured at 290 mμ in 1-cm cells

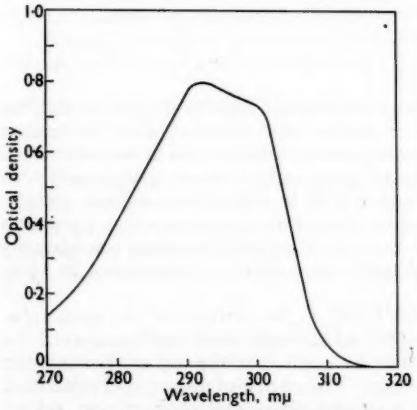

Fig. 7. Absorption spectrum of 2:4:5-trichlorophenol (m.p. 67·5°C) at a concentration of 0·005 per cent. w/v in analytical-reagent grade methanol. Measurements were made with a Unicam SP500 spectrophotometer with 1-cm cells

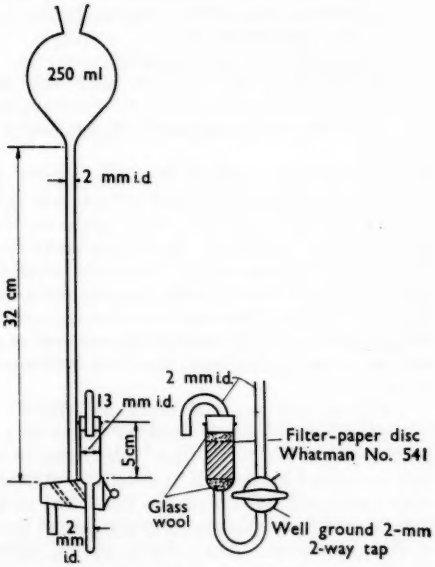

Fig. 8. Ion-exchange column

DETERMINATION OF THE 2:4:5- ISOMER—

The determination of the 2:4:5- isomer in the effluent (with the 0·2 per cent. v/v solution of acetic acid in methanol) may be completed by at least two methods—

(*a*) *Ultra-violet absorption method*—The effluent may be diluted to a standard volume (250 ml) and the ultra-violet absorption of the solution determined at the peak wavelength (292 mμ, see Fig. 7) for pure 2:4:5-trichlorophenol. By comparison of this measurement

with that of a standard solution (20 mg per 250 ml) of the pure isomer (in a 0·2 per cent. v/v solution of acetic acid in methanol), the percentage of 2:4:5- isomer in the original sample may be calculated.

(*b*) *Titration method*—When an ultra-violet spectrophotometer is not available, the determination may be completed in the following manner. The effluent is made alkaline by adding sodium hydroxide solution in slight excess and is evaporated to dryness on a steam-bath to remove the methanol. The residue is then dissolved in distilled water and the 2:4:5- isomer is titrated by the bromination method of Koppeschaar.[2] The only point of note in this procedure is the use of the steam-bath for evaporation of the alkaline solution; it is essential that the residue should not be overheated (as may occur on a hot-plate), since considerable decomposition occurs and low results will be obtained.

Method

Apparatus—

Ion-exchange column—As shown in Fig. 8, this design of column has been found extremely useful for routine analysis. The long capillary stem increases the head of liquid and permits higher rates of flow without applying external pressure. The two-way tap allows rapid and thorough cleaning of the reservoir to be carried out without being restricted by the rate of flow through the column.

Unicam SP500 spectrophotometer.

Reagents—

Acetic acid, glacial—Analytical-reagent grade.
De-Acidite FF (chloride form)—The material having an average particle size of 50 μ.
Sodium acetate solution, 10 per cent. w/v—Prepare this from crystalline sodium acetate.
Hydrochloric acid, concentrated—Analytical-reagent grade.
Methanol—Analytical-reagent grade.
Sodium hydroxide, N.
Sodium thiosulphate, 0·01 N.
Starch indicator—A 1 per cent. w/v freshly prepared solution.
Potassium bromate, 0·01 N—Containing 5 g of potassium bromide per litre.
Potassium iodide solution, 20 per cent. w/v.

Procedure for preparing the column of resin—

The material as supplied, which is in the chloride form, should first be steeped in distilled water overnight and then thoroughly washed by decantation with distilled water to remove the very fine particles. Pack the resin in a fairly wide-bore tube (1·5 to 2 cm) and wash it with the sodium acetate solution until the effluent gives only a faint opalescence with silver nitrate. Then wash the resin with distilled water until it is free from sodium acetate. Remove the washed resin from the tube and wash it by decantation with successive portions of methanol until it is free from excess of moisture—the rate of settling increases considerably and approximately 5 g of the final material should settle from 100 ml of methanol in 1½ to 2 minutes.

Fill the column with methanol, place a glass-wool plug at the bottom of the resin tube, taking care to avoid air bubbles, and add a thick slurry of the resin with methanol until the settled height is 30 $\pm$ 1 mm. Very gentle suction may be applied at the top of the reservoir and controlled by the tap to assist the settling of the resin. Place a disc of filter-paper moistened with methanol on top of the resin bed and insert a second glass-wool plug on top, taking care to avoid air bubbles. Finally, insert the outlet tube, which should press lightly on the top of the glass-wool. The column should allow a rate of flow of 3 ml per minute. If the rate of flow is slower than this, tip out the resin and re-wash it with methanol until it has a slightly shorter settling time.

Procedure for the ion-exchange separation—

Weigh out 0·2500 g of commercial 2:4:5-trichlorophenol, dissolve it in methanol and transfer to a clean dry 250-ml calibrated flask and dilute to the mark with methanol. By pipette put a 20-ml aliquot into the reservoir of the prepared column, place a 400-ml beaker below the outlet tube and pass the sample through the column at 3 ml per minute, allowing the liquid level to fall to the top of the capillary stem. Rinse the reservoir with 10 ml of

a 0·02 per cent. v/v solution of acetic acid in methanol and pass the solution through the column at 3 ml per minute, allowing the liquid level to fall to the top of the capillary tube. Repeat the rinsing procedure twice. Add 200 ml of the 0·02 per cent. v/v solution of acetic acid in methanol to the reservoir and pass it through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary stem. The total volume of effluent should be 250 ml; which should be discarded. Turn the tap to the waste position and rinse the reservoir with a 0·2 per cent. v/v solution of acetic acid in methanol, allow the rinsings to drain to waste and leave the liquid level at the top of the capillary stem. Place a clean 400-ml beaker below the outlet tube, add 200 ml of the 0·2 per cent. v/v solution of acetic acid in methanol to the reservoir and pass it through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary stem. Collect all the effluent and proceed in one of the following ways, depending on the equipment available.

(*a*) *Ultra-violet absorption method*—Transfer the effluent to a clean dry 250-ml calibrated flask and dilute it to the mark with a 0·2 per cent. v/v solution of acetic acid in methanol.

Prepare a standard solution containing 20 mg of pure 2:4:5-trichlorophenol in 250 ml of a 0·2 per cent. v/v solution of acetic acid in methanol.

Measure the absorption of both sample solution and standard at 292 mμ in 1-cm cells, using the solvent as a blank. If the absorptions obtained are S and P, respectively, then the percentage of 2:4:5- isomer is given by 100 S/P.

(*b*) *Titration method*—Add 10 ml of N sodium hydroxide to the effluent and evaporate to dryness on a steam-bath. Dissolve the residue in distilled water and transfer the solution to a standard iodine titration flask. Add 25·0 ml of 0·01 N potassium bromate, mix, add 15 ml of concentrated hydrochloric acid, replace the stopper quickly, seal the neck of the flask with 20 per cent. potassium iodide solution, mix, and commence timing the bromination period of 5 minutes by means of a stopwatch. The brominated phenol is precipitated. At the end of 5 minutes, remove the stopper, add 10 ml of 20 per cent. potassium iodide solution, replace the stopper and mix thoroughly until all the excess of bromine has been absorbed. Rinse and remove the stopper, and titrate the liberated iodine with 0·01 N sodium thiosulphate until the solution is pale yellow. Add 5 ml of starch indicator and continue the titration slowly to the end-point (x ml).

Repeat the entire procedure, including the ion-exchange separation, but omitting the sample, and record the titre obtained (y ml).

$$\text{Then, 2:4:5- isomer, per cent.} = \frac{(y - x) \times 0{\cdot}9875}{20} \times 100.$$

PROCEDURE FOR REGENERATING THE COLUMNS OF RESIN—

The columns can be used repeatedly if the 2:3:6- isomer left on the column is removed. Fill the reservoir with 200 ml of a 5 per cent. v/v solution of acetic acid in methanol and pass it through the column at 3 ml per minute. Rinse the reservoir thoroughly with methanol, allowing the rinsings to drain to waste; refill the reservoir with 200 ml of methanol and pass it through the column at 3 ml per minute. The column is then ready for the next sample.

RESULTS AND DISCUSSION

Several samples obtained from British and German sources were analysed by the ion-exchange titration method and the infra-red absorption method. The results are shown in Table I.

TABLE I

ANALYSIS OF COMMERCIAL 2:4:5-TRICHLOROPHENOL

Sample No.	2:4:5-Trichlorophenol found by— ion-exchange titration method, %	infra-red method, %
1	84·5	81 ± 2
2	83·1	82 ± 2
3	84·5, 83·6	85 ± 2
4	93·8	93·3 ± 1
5*	78·8, 80·4	79 ± 2

* German.

The ion-exchange method tends to give slightly higher results than the infra-red method, but the agreement between the two methods is satisfactory for routine analysis of this type of material. The ion-exchange titration method requires very little in the way of special equipment and is particularly suitable for control laboratories.

Conclusions

The method described provides a simple, rapid and accurate routine method for the determination of the 2:4:5- isomer in commercial 2:4:5-trichlorophenol. The ion-exchange separation by means of non-aqueous solvents constitutes a radically different approach to the analysis of weakly acidic aromatic compounds. The technique can obviously be developed considerably, and its application to the analysis of commercial 2:4-dichlorophenol is described in Part II.

Part II. Analysis of Commercial 2:4-Dichlorophenol

Some success had already been achieved in the analysis of samples of 2:4-dichlorophenol by the partition-chromatographic method of Freeman, Gardner and Pound.[3] The impurities detected by this method were *p*-chlorophenol, 2:6-dichlorophenol and 2:4:6-trichlorophenol. The conditions required for the separation of these impurities were very critical and only a partial separation of the 2:4- and 2:6- isomers was achieved under the best conditions. Extreme care in the preparation of the partition column was essential, temperature changes produced significant effects and the maximum loading of the column was only 4 mg; this last condition severely restricts the limits of detection of the impurities.

It was considered, in view of the work carried out on 2:4:5-trichlorophenol, that more satisfactory results might be possible by graded-elution ion-exchange chromatography.

Experimental

Behaviour of 2:4-dichlorophenol and impurities on a large column—

A preliminary study of the behaviour of *p*-chlorophenol, 2:4-dichlorophenol, 2:6-dichlorophenol and 2:4:6-trichlorophenol was carried out with a large ion-exchange column

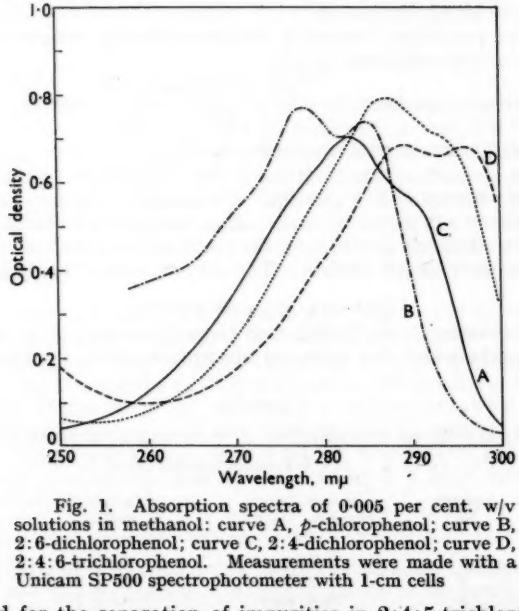

Fig. 1. Absorption spectra of 0·005 per cent. w/v solutions in methanol: curve A, *p*-chlorophenol; curve B, 2:6-dichlorophenol; curve C, 2:4-dichlorophenol; curve D, 2:4:6-trichlorophenol. Measurements were made with a Unicam SP500 spectrophotometer with 1-cm cells

similar to that used for the separation of impurities in 2:4:5-trichlorophenol (see Part I), *viz.*, a column, 16 mm × 160 mm, of 100 to 200-mesh B.S.S. De-Acidite FF (acetate form), with methanol as solvent and a rate of flow of 1·5 ml per sq. cm per minute.

A synthetic solution containing 0·1 per cent. w/v of each of the above-mentioned phenols was prepared in methanol. The ultra-violet absorption spectra of these phenols in methanol are shown in Fig. 1.

A 5-ml aliquot of the synthetic solution (*i.e.*, a total loading of 20 mg) was transferred to the column and a graded elution was carried out with (*a*) methanol, (*b*) a 0·2 per cent. v/v solution of acetic acid in methanol and (*c*) a 1 per cent. v/v solution of acetic acid in methanol. The effluents were shown to contain (*a*) *p*-chlorophenol, (*b*) 2:4- and 2:6-dichlorophenol and (*c*) 2:4:6-trichlorophenol. A typical elution graph is shown in Fig. 2.

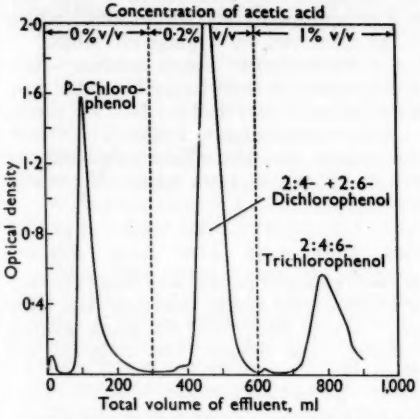

Fig. 2. Graded elution of a synthetic mixture of phenols on a 16-mm × 160-mm column of 100 to 200-mesh B.S.S. De-Acidite FF; solvent, methanol; rate of flow, 1·5 ml per sq. cm per minute. The optical densities were measured at 285 mμ in 1-cm cells

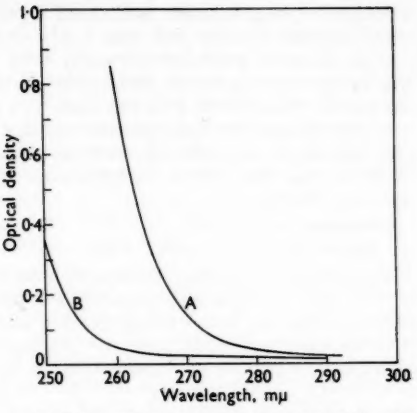

Fig 3. Absorption spectra of triethylamine in methanol: curve A, 10 per cent. v/v of triethylamine; curve B, 10 per cent. v/v of triethylamine and 10 per cent. v/v of acetic acid. Measurements were made with a Unicam SP500 spectrophotometer with 1-cm cells

The conditions in the column were very stable and a loading of 100 mg of crude 2:4-dichlorophenol could be employed; this gave very good limits of detection for the *p*-chlorophenol and 2:4:6-trichlorophenol impurities. No separation of the 2:4- and 2:6- isomers was achieved, however, and, as with 2:4:5-trichlorophenol, the elutions on this size of column required a considerable length of time.

Effect of pH and use of small columns—

A fresh approach to the problem was sought and consideration was given to the effect of pH on the ion-exchange separation. On theoretical grounds a certain pH exists at which the difference in degree of dissociation of any pair of phenols is at a maximum. This condition should give the best possible separation by ion-exchange.

Also, in connection with other unpublished work, it had been found that triethylamine salts could be used to prepare buffer solutions in methanol of definite pH value. These salts are freely soluble in methanol and the ultra-violet absorption at moderate concentrations does not interfere with the photometric determination of any of the phenols at present under consideration. The triethylamine used was freshly distilled and had an absorption of 0·67 at 290 mμ in 1-cm cells; the complete spectrum of a 10 per cent. v/v solution in methanol is shown in Fig. 3. The effect on the spectrum of the addition of a 10 per cent. v/v solution of acetic acid is also shown in Fig. 3 for comparison. The "cut-off" value is shifted to lower wavelengths and the background absorption in the range 270 mμ to 300 mμ is reduced to a stable level that enables the "triethylamine acetate" solutions to be employed as blanks.

In order to examine the effect of using such buffer solutions and reduce the time factor, the column size was reduced to that employed in the final method for the determination of 2:4:5-trichlorophenol, *viz.*, a 13-mm × 30-mm column of De-Acidite FF (acetate form), of average particle size 50 μ, with methanol as solvent and a rate of flow of 3 ml per minute.

ABSORPTION OF 2:4- AND 2:6- ISOMERS ON A SMALL COLUMN—

A synthetic solution containing 0·1 per cent. w/v of each of the 2:4- and 2:6- isomers was prepared in methanol. A 5-ml aliquot of this solution was transferred to the column, which was then rinsed with methanol. Absorption measurements on the effluent showed that the retention of the phenols was quantitative.

ELUTION WITH TRIETHYLAMINE - ACETIC ACID BUFFERS—

A stock solution of "triethylamine acetate" was prepared by dissolving 69·9 ml of triethylamine and 28·6 ml of glacial acetic acid in methanol and diluting to 1 litre with methanol. This solution contained 8 per cent. w/v or approximately 10 per cent. v/v of triethylamine acetate and had a pH of $8{\cdot}0 \pm 0{\cdot}1$, as measured by a glass electrode.

(*a*) *Elution with approximately* 0·02 *per cent. v/v triethylamine acetate solution*—As it was known from previous work (Part I) that 2:4-dichlorophenol could easily be eluted from the small column with 0·02 per cent. v/v acetic acid solution, it was decided to try a similar concentration of triethylamine acetate in methanol. The stock solution was diluted (1 + 499), and 100 ml of this solution were passed through the column, and the effluent was collected in 10-ml fractions whose absorptions were measured at 285 mμ in 1-cm cells. The results were as follows—

Fraction No. ..	1	2	3	4	5	6	7	8	9	10
Absorption ..	0·032	0·063	0·077	0·086	0·093	0·107	0·118	0·128	0·135	0·145

The gradually increasing absorption indicated that a slow release of phenol was being effected.

(*b*) *Elution with approximately* 0·2 *per cent. v/v triethylamine acetate solution*—The effect of increasing the buffer concentration was examined. A new dilution of the stock solution (1 + 49) was prepared and the elution was continued. The effluent was collected and measured as before, the absorptions being as follows—

Fraction No...	1	2	3	4	5	6	7	8
Absorption ..	0·453	1·078	1·412	1·440	0·920	0·410	0·166	0·072
Fraction No...	9	10	11	12	13	14	15	
Absorption ..	0·033	0·015	0·004	0·002	0	0	0	

A rapid and complete release of phenol was obtained. A useful convention was introduced to permit a rapid assessment to be made of the amount of phenol concerned in any particular elution. Consider, for example, the absorption of 5 mg of 2:4-dichlorophenol in 100 ml of a 0·2 per cent. solution of triethylamine acetate in methanol. The absorption of this solution at 288 mμ in 1-cm cells is 0·772. If the 5 mg were now concentrated in 10 ml of solution, the equivalent theoretical absorption would be 7·72. As the effluent was collected in 10-ml fractions, the sum of all the absorption measurements is equivalent to the theoretical absorption of the total amount of phenol dissolved in a volume of 10 ml.

The sum of all the measurements obtained in the above-mentioned elutions is approximately 7, whereas the equivalent theoretical absorption for the 10-mg load originally applied to the column would be approximately 14. This result, together with the fact that the absorptions in the 0·2 per cent. v/v triethylamine acetate elution decrease to zero, indicated that a separation had actually been effected.

(*c*) *Elution with a* 0·2 *per cent. v/v solution of acetic acid in methanol*—Confirmation of this separation was obtained by continuing the elution with a 0·2 per cent. v/v solution of acetic acid in methanol (pH 3·5, arbitrarily chosen acid conditions). A rapid release of the second phenol was obtained, as shown by the following absorptions, the equivalent theoretical absorption value of these fractions (10 ml) being again approximately 7—

Fraction No. ..	1	2	3	4	5	6	7	8	9	10
Absorption ..	0·76	1·63	2·7	1·32	0·40	0·19	0·05	0·005	0·003	0

An examination of the ultra-violet absorption spectrum of the phenol eluted with the 0·2 per cent. v/v acetic acid solution identified this phenol as the pure 2:6- isomer. A complete separation of the 2:4- and 2:6- isomers was therefore obtained under the conditions described above.

DEVELOPMENT OF THE METHOD

The technique of varying the pH of the eluting medium was obviously capable of considerable development. A series of experiments was therefore carried out to establish the

conditions required for the complete analysis of a mixture of *p*-chlorophenol, 2:4- and 2:6-dichlorophenols and 2:4:6-trichlorophenol, with use of the small column described above.

BEHAVIOUR OF 2:4-DICHLOROPHENOL ON A SMALL COLUMN—

As the samples were normally prepared in methanol, it was desirable to find the maximum loading that could be quantitatively absorbed on the small column.

(*a*) *Maximum loading*—A solution of 2:4-dichlorophenol was prepared at a concentration of 0·1 per cent. w/v in methanol (equivalent theoretical absorption value 14) and this was run continuously through the column. The effluent was collected in 10-ml fractions and the absorptions were measured at 288 mμ (the peak wavelength) in 1-cm cells; the results were as follows—

Fraction No.	1	2	3	4
Absorption	0·098	0·110	1·96	>3
Loading, mg	10	20	30	40

The "break-through" capacity was only 20 ml, *i.e.*, 20 mg, for this solution.

(*b*) *Effect of pH*—It was considered, on theoretical grounds, that the break-through capacity could be increased by raising the pH of the solution.

A new solution of 2:4-dichlorophenol was prepared at a concentration of 0·1 per cent. w/v in a 0·2 per cent. v/v solution of triethylamine in methanol; the pH of this solution was 9·2.

When this solution was run continuously through the column, no evidence of 2:4-dichlorophenol was found in the effluent up to a total volume of at least 140 ml (*i.e.*, 140 mg loading). The absorption of the effluent remained constant at 0·016. A distinctly visible pale band appeared on the resin during this experiment and it progressively broadened as the experiment proceeded. At 140 ml of volume of effluent this band occupied only about half of the resin column; the break-through capacity on this basis must be about 250 to 300 mg.

It was therefore established that the small column could be loaded safely with, say, 100 mg of 2:4-dichlorophenol in a solution of pH 9·2, *i.e.*, in a 0·2 per cent. v/v solution of triethylamine in methanol.

BEHAVIOUR OF 2:6-DICHLOROPHENOL ON A SMALL COLUMN—

If the column were loaded with 100 mg of crude 2:4-dichlorophenol at pH 9·2, the 2:4-isomer should be capable of subsequent elution at pH 8·0 (see the original experimental work, p. 572), the 2:6- isomer being left on the column. As 100 mg of 2:4- isomer would require a considerable amount of eluting agent to remove it from the column, it was felt that the procedure might be shortened in the following manner. If the crude sample were prepared in a solution of pH 8·0, the retention of most of the 2:4- isomer would be prevented and this procedure might still leave the 2:6- isomer on the column. Two points required examination; first, to show that the 2:6- isomer was retained on the column from solutions of pH 8·0 and, secondly, to determine how much more of the solution of pH 8·0 was required to remove the residual 2:4- isomer from the column.

(*a*) *Absorption of 2:6-dichlorophenol at pH* 8·0—A solution of 2:6-dichlorophenol was prepared in a 0·2 per cent. v/v solution of triethylamine acetate in methanol (pH 8·0) at a concentration of 0·1 per cent. w/v. This solution was run continuously through the column, the effluent being collected in 10-ml fractions and measured at 285 mμ in 1-cm cells; the absorptions were as follows—

Fraction No.	1	2	3	4	5	6	7	8	9	10
Absorption	0·019	0·087	0·149	0·158	0·160	0·163	0·163	0·181	0·228	0·374
Loading, mg	10	20	30	40	50	60	70	80	90	100

A "frontal" analysis was obtained; the "constant" value obtained in fractions 3 to 7 was due to the presence of 2:4-dichlorophenol as an impurity in the sample of 2:6-dichlorophenol. The amount of this impurity may be calculated from the constant value and is about 1 per cent. of the original sample.

The increasing absorption from fraction 8 onwards was due to the break-through of 2:6-dichlorophenol and the break-through capacity of the column under these conditions is therefore about 70 mg of the 2:6- isomer.

If, therefore, the sample of 2:4-dichlorophenol is dissolved in a 0·2 per cent. v/v solution of triethylamine acetate in methanol, this solution may be run continuously through the

column without leakage of the 2:6-dichlorophenol impurity until about 70 mg of the impurity have accumulated. It should be noted, of course, that the 2:6- isomer can be accurately determined by accumulating only 2 to 5 mg, and it is, therefore, not necessary to run the column to its break-through capacity. This technique obviously increases enormously the sensitivity of the method and should permit very small amounts of impurity to be accurately determined.

(*b*) *Removal of residual 2:4-dichlorophenol*—A solution of 2:4-dichlorophenol was prepared in a 0·2 per cent. v/v solution of triethylamine acetate in methanol at a concentration of 0·1 per cent. w/v. One hundred millilitres of this solution were run through the column and the effluent was discarded. The column was then eluted with a further 200 ml of a 0·2 per cent. v/v solution of triethylamine acetate in methanol, and 10-ml fractions were collected and their absorptions were measured at 288 mμ in 1-cm cells, the results being as follows—

Fraction No.	1 to 9	10	11	12	13	14	15	16	17	18	19	20
Absorption ..	All >3	1·4	0·510	0·166	0·058	0·015	0·002	0	0	0	0	0

A considerable amount of 2:4-dichlorophenol was retained on the column under these conditions, but its removal was completely effected with 200 ml of wash solution.

(*c*) *Tentative method for the determination of the 2:6- isomer*—A tentative procedure could now be proposed for the separation and determination of the 2:6- isomer from 100-mg samples of 2:4-dichlorophenol, as follows—

> One hundred millilitres of sample solution containing 0·1 per cent. w/v of 2:4-dichlorophenol in a 0·2 per cent. v/v solution of triethylamine acetate in methanol are run through the column, the residual 2:4-dichlorophenol on the column is removed by washing with 200 ml of a 0·2 per cent. v/v solution of triethylamine acetate in methanol and the 2:6- isomer is finally recovered by eluting the column with 100 ml* of a 0·2 per cent. v/v solution of acetic acid in methanol. The determination is then completed by measuring the ultra-violet absorption of the acid effluent.

The procedure was carried out on the best available commercial (distilled) 2:4-dichlorophenol (setting point, 40·7° C); this material had been examined previously by the graded-elution method with acetic acid on the large column and shown to contain only 0·3 per cent. of *p*-chlorophenol and less than 0·1 per cent. of 2:4:6-trichlorophenol.

Two separate small columns were examined at the same time and the last 100 ml of washings from each column (with a 0·2 per cent. v/v solution of triethylamine acetate in methanol) were examined to ensure complete removal of the 2:4- isomer. The absorptions obtained for 10-ml fractions of these washings at 288 mμ in 1-cm cells were as follows—

Fraction No.	10	11	12	13	14	15 to 20
Absorption (column 1)	0·95	0·125	0·046	0·015	0·002	0
Absorption (column 2)	0·002	0	0	0	0	0

Both columns were completely freed from the 2:4- isomer with 150 ml of wash solution.

The 100 ml of 0·2 per cent. v/v acetic acid effluent were collected in bulk and the absorptions of portions were measured at 285 mμ (the peak wavelength) in 1-cm cells. Absorptions of 0·568 and 0·570 were obtained, these corresponding, respectively, to 3·82 and 3·84 per cent. of the 2:6- isomer.

The ultra-violet absorption spectrum of the acid effluent was examined and identified as that of pure 2:6-dichlorophenol.

The conditions for the quantitative separation and determination of 2:6-dichlorophenol in 100 mg of 2:4-dichlorophenol by means of the small column were therefore established.

BEHAVIOUR OF 2:4:6-TRICHLOROPHENOL ON A SMALL COLUMN—

The two points of interest were, first, whether the 2:4:6-trichlorophenol could be eluted from the column at pH 8·0 (a 0·2 per cent. v/v solution of triethylamine acetate) and, secondly, if not, whether the 2:6-dichlorophenol and 2:4:6-trichlorophenol retained on the column could be separated for individual determination. A synthetic solution of 2:4:6-trichlorophenol was prepared at a concentration of 0·1 per cent. w/v in methanol. A 5-ml aliquot of this solution was transferred to the column and the column was rinsed with methanol. The absorption was quantitative.

* This volume completely removes the 2:6- isomer from the column, as shown in the original experimental work (see p. 572).

(*a*) *Attempted elution of* 2:4:6-*trichlorophenol at pH* 8·0—The column was washed with a 0·2 per cent. v/v solution of triethylamine acetate in methanol, and 10-ml fractions were collected and their absorptions were measured at 296 mμ (the peak wavelength) in 1-cm cells. No evidence of 2:4:6-trichlorophenol was found in the first 200 ml of effluent.

(*b*) *Elution with a* 0·2 *per cent. v/v solution of acetic acid in methanol*—The elution was continued with a 0·2 per cent. v/v solution of acetic acid in methanol, and 10-ml fractions were collected and their absorptions were measured as before, the results being as follows—

Fraction No.	1	2	3	4	5	6	7	8	9
Absorption	0·007	0·010	0·005	0·006	0·005	0·016	0·006	—	—

Fraction No.	10	11	12	13	14	15
Absorption	0·005	0·008	0·014	0·046	0·107	0·222

There was no release of 2:4:6-trichlorophenol in the first 100 ml of effluent, so that 2:6-dichlorophenol and 2:4:6-trichlorophenol can easily be separated by this elution (compare with the results for the 0·2 per cent. v/v acetic acid solution, p. 572).

(*c*) *Elution with a* 5 *per cent. v/v solution of acetic acid in methanol*—The 2:4:6-trichlorophenol was slowly eluted from fraction 12 (*i.e.*, 120 ml) onwards, but to complete the elution in a volume suitable for the determination of the 2:4:6-trichlorophenol, the concentration of acetic acid was increased to 5 per cent. v/v. Again, 10-ml fractions were collected and the absorptions were measured as before, the results being as follows—

Fraction No.	1	2	3	4	5	6	7	8	9	10
Absorption	>3	>3	0·315	0·089	0·034	0·024	0·017	0·042	0·025	0·015

A rapid and complete removal of 2:4:6-trichlorophenol was achieved with a total volume of 100 ml. A trace of another phenol (an impurity) in the sample is indicated in fraction 8.

The conditions for the separation and determination of the components of a mixture of 2:4- and 2:6-dichlorophenols and 2:4:6-trichlorophenol are now established.

BEHAVIOUR OF *p*-CHLOROPHENOL ON A SMALL COLUMN—

Here the points of interest were, first, whether *p*-chlorophenol could be quantitatively absorbed at high pH as with 2:4-dichlorophenol and, secondly, if so, whether the *p*-chlorophenol could be selectively eluted from the column without removal of 2:4-dichlorophenol even at loadings of 100 mg.

(*a*) *Absorption of* p-*chlorophenol at high pH*—A synthetic solution of *p*-chlorophenol was prepared at a concentration of 0·1 per cent. w/v in a 0·2 per cent. v/v solution of triethylamine in methanol. The pH of this solution was 9·2, and a 5-ml aliquot was transferred to the column, which had previously been rinsed with a 0·2 per cent. v/v solution of triethylamine in methanol to maintain a high pH. The column was then washed with a further 100 ml of a 0·2 per cent. v/v solution of triethylamine in methanol (pH 9·8), and 10-ml fractions were collected and their absorptions were measured at 283 mμ (the peak wavelength) in 1-cm cells. The *p*-chlorophenol was quantitatively retained by the resin and was not eluted with 100 ml of a 0·2 per cent. v/v solution of triethylamine in methanol.

(*b*) *Elution with "composite" solution*—It was thought at this stage that if a high pH was maintained and a small amount of acetate ion introduced, the removal of the *p*-chlorophenol might be effected without the removal of any 2:4-dichlorophenol from the column. A "composite" solution was prepared by diluting 200 ml of a 0·2 per cent. v/v solution of triethylamine acetate in methanol to 1 litre with a 0·2 per cent. v/v solution of triethylamine in methanol; the pH of this solution was 8·6.

The elution of the column was continued with this "composite" solution, and 10-ml fractions were collected and their absorptions were measured as before, the results being as follows—

Fraction No.	1	2	3	4	5	6	7	8	9	10
Absorption	0·009	0·035	0·089	0·161	0·259	0·363	0·452	0·550	0·660	0·728

Fraction No.	11	12	13	14	15	16	17	18	19	20
Absorption	0·792	0·895	0·908	0·800	0·297	0·057	0·010	0·003	0	0

Complete removal of the *p*-chlorophenol was effected by this solution. The shape of the elution peak was unusual in that the "trailing" edge was extremely sharp. This effect was due to the high pH of the eluting medium.

BEHAVIOUR OF A MIXTURE OF *p*-CHLOROPHENOL AND 2:4-DICHLOROPHENOL—

It was now necessary to check whether this "composite" solution would selectively elute *p*-chlorophenol in the presence of loadings of 100 mg of 2:4-dichlorophenol.

(*a*) *Absorption of the mixture at high pH values*—A synthetic solution was prepared containing 0·1 per cent. w/v of 2:4-dichlorophenol and 0·005 per cent. w/v of *p*-chlorophenol in a 0·2 per cent. v/v solution of triethylamine in methanol. One hundred millilitres of this solution were run through the column, and 10-ml fractions were collected and their absorptions were measured at 283 mμ in 1-cm cells, the results being as follows—

Fraction No.	1	2	3	4	5	6	7	8	9	10
Absorption	0·011	0·372	0·714	0·733	0·739	0·742	0·742	0·742	0·742	0·742

A "frontal" analysis was obtained, the *p*-chlorophenol passing through the column under these conditions. This rather unexpected result is easily explained in the following manner. It was shown in the experiments described under 2:4-dichlorophenol (p. 573) that 2:4-dichlorophenol was completely retained from a 0·2 per cent. v/v solution of triethylamine in methanol. But, during the absorption of the 2:4-dichlorophenol, the equivalent amount of acetic acid is released into the effluent, which becomes in effect a mixture of triethylamine acetate and triethylamine. Calculation showed that this effluent corresponded fairly closely to the "composite" solution employed for the elution of *p*-chlorophenol.

The *p*-chlorophenol may be calculated from the constant absorption value obtained in fractions 6 to 10 and corresponds to 0·0053 per cent. w/v in the original solution. The additional amount (0·0003 per cent.) is derived from the 2:4-dichlorophenol employed, and is equivalent to 0·3 per cent. of impurity in the solid sample of 2:4-dichlorophenol.

A further 250 ml of "composite" solution were run through the column, but no 2:4-dichlorophenol was eluted.

Two main facts were established, first, that *p*-chlorophenol could be selectively eluted from the column with the "composite" solution without removal of 2:4-dichlorophenol even at loadings of 100 mg and, secondly, that the determination of *p*-chlorophenol could be carried out by frontal analyses at large loadings of sample and high pH.

DISCUSSION OF EXPERIMENTAL RESULTS—

From the results obtained by all these experiments, it is possible to propose three simple systems for the complete analysis of crude 2:4-dichlorophenol.

(*a*) *Determination of* 2:4- *isomer*—The sample is prepared at a concentration of 0·1 per cent. w/v in a 0·2 per cent. v/v solution of triethylamine in methanol (high pH) and a 10-ml aliquot (*i.e.*, a loading of 10 mg) was taken for analysis. The entire sample is quantitatively absorbed under these conditions. The *p*-chlorophenol is removed by elution with the "composite" solution described previously. The 2:4- isomer is then eluted at pH 8 with a 0·2 per cent. v/v solution of triethylamine acetate in methanol to leave the 2:6- isomer and 2:4:6-trichlorophenol on the column. The 2:4- isomer is determined by measuring the ultra-violet absorption of the effluent from the elution with the 0·2 per cent. v/v solution of triethylamine acetate in methanol.

(*b*) *Determination of* 2:6- *isomer and* 2:4:6-*trichlorophenol*—Here a large sample weight is employed, the sample is prepared at a concentration of 0·1 per cent. w/v in a 0·2 per cent. v/v solution of triethylamine acetate in methanol and 100 ml of this solution (*i.e.*, a loading of 100 mg) is taken for analysis. The 2:6- isomer and the 2:4:6-trichlorophenol are retained quantitatively on the column. Residual amounts of the 2:4- isomer are removed by eluting with 200 ml of a 0·2 per cent. v/v solution of triethylamine acetate in methanol. The 2:6- isomer and the 2:4:6-trichlorophenol are then eluted individually by graded elution with 0·2 per cent. v/v and 5 per cent. v/v solutions of acetic acid in methanol and determined by ultra-violet absorption measurements.

(*c*) *Determination of* p-*chlorophenol*—Again a large sample weight is employed, but the sample is prepared at a concentration of 0·1 per cent. w/v in a 0·2 per cent. v/v solution of triethylamine in methanol (as for the determination of the 2:4- isomer). The sample solution is run through the column continuously until the break-through of *p*-chlorophenol gives a constant value of the ultra-violet absorption. The *p*-chlorophenol is calculated from this constant value.

These systems may be run simultaneously on three separate columns and the total time required for the determination of all the components is 3 to 4 hours.

Method

Apparatus—

Ion-exchange column—As required in Part I (see p. 568).
Unicam SP500 spectrophotometer.

Reagents—

Acetic acid, glacial—Analytical-reagent grade.
De-Acidite FF (chloride form)—The material having an average particle size of 50 μ.
Methanol—Analytical-reagent grade.
Triethylamine—Freshly distilled.
Acetic acid solution in methanol, 0·2 per cent. v/v.
Acetic acid solution in methanol, 5·0 per cent. v/v.
Stock triethylamine acetate solution in methanol—Dissolve 69·9 ml of triethylamine and 28·6 ml of glacial acetic acid in methanol and dilute to 1 litre with methanol.
Dilute triethylamine acetate solution in methanol—Dilute 20 ml of the stock solution to 1 litre with methanol.
Triethylamine solution in methanol, 0·2 per cent. v/v.
"Composite" solution—Dilute 200 ml of the dilute triethylamine acetate solution in methanol to 1 litre with 0·2 per cent. v/v solution of triethylamine in methanol.

Procedure for preparing solutions of the sample—

(*a*) *Solution I*—Accurately weigh 0·500 g of sample, dissolve it in the 0·2 per cent. v/v solution of triethylamine in methanol and dilute accurately to 500 ml with the same solution.

(*b*) *Solution II*—Accurately weigh out 0·500 g of sample, dissolve it in the dilute triethylamine acetate solution in methanol and dilute accurately to 500 ml with the same solution.

Note—

Samples of 2:4-dichlorophenol that have been melted and run into sample bottles tend to be non-uniform. A representative sample may be ensured by the following procedure. Use a No. 10 or No. 11 cork-borer and remove several (4 to 6) "cores" from the bulk sample, break up the "cores," mix thoroughly and weigh out required amounts from this material.

Procedure for preparing the column of resin—

The procedure described under "Method" (Part I, p. 568) may be followed. The alternative procedure described below is shorter and more direct, but is rather more expensive owing to the reagents used.

Allow the resin (in the chloride form) to steep overnight in distilled water and then wash it thoroughly by decantation with distilled water to remove the very fine particles. Then wash the resin by decantation with successive portions of methanol to remove the excess of moisture—the rate of settling increases considerably and approximately 5 g of the final material should settle from 100 ml of methanol in 1½ to 2 minutes. Pack this material in the column, as described on p. 568. Convert the resin to the acetate form by washing it with the stock solution of triethylamine acetate in methanol until only a faint opalescence is obtained in the effluent after acidification with nitric acid and treatment with silver nitrate. Wash the resin with 200 ml of the 5 per cent. v/v solution of acetic acid in methanol and finally with methanol until free from acid. The column is then ready for use.

Procedure for determining the 2:4- isomer—

Rinse the reservoir of the prepared column with three 10-ml portions of "composite" solution. Allow the rinsings to drain through the column and discard the effluent; let the liquid level fall to the top of the capillary stem. By pipette put a 10-ml aliquot of sample solution I into the reservoir, allow it to drain through the column at 3 ml per minute; let the liquid level fall to the top of the capillary stem and discard the effluent. Rinse the reservoir with 10 ml of the "composite" solution, allow it to drain through the column at 3 ml per minute; let the liquid level fall to the top of the capillary stem and discard the effluent. Repeat the rinsing procedure twice more. Add 170 ml of "composite" solution

to the reservoir, allow it to drain through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary stem; discard the effluent. Rinse the reservoir with three 10-ml portions of the dilute solution of triethylamine acetate in methanol and allow the rinsings to drain to waste; leave the capillary stem filled with liquid. Add 150 ml of the dilute solution of triethylamine acetate in methanol to the reservoir, place a clean dry 200-ml calibrated flask below the outlet tube and allow the solution to drain through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary. Dilute the effluent accurately to 200 ml with the dilute solution of triethylamine acetate in methanol. Measure the absorption at 288 mμ in a 1-cm cell, using the dilute solution of triethylamine acetate in methanol as the blank.

If A is the absorption of the unknown at 288 mμ in a 1-cm cell with a final volume of effluent of 200 ml, and as the absorption for 10 mg of pure 2:4-dichlorophenol in 200 ml at 288 mμ in a 1-cm cell is 0·772, then—

$$2:4\text{- isomer, per cent.} = \frac{A}{0{\cdot}772} \times 100.$$

PROCEDURE FOR DETERMINING THE 2:6- ISOMER AND 2:4:6-TRICHLOROPHENOL—

Add 100 ml of sample solution II to the reservoir of a clean column, allow it to drain through the column at 3 ml per minute; let the liquid level fall to the top of the capillary and discard the effluent. Rinse the reservoir with 10 ml of the dilute solution of triethylamine acetate in methanol, and allow it to drain through the column at 3 ml per minute; let the liquid level fall to the top of the capillary and discard the effluent. Repeat the rinsing procedure twice more. Add 200 ml of the dilute solution of triethylamine acetate in methanol to the reservoir, allow it to drain through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary, discard the effluent. Rinse the reservoir with four 10-ml portions of methanol, allow the rinsings to drain to waste, and leave the capillary filled with methanol. Add 95 ml of the 0·2 per cent. v/v solution of acetic acid in methanol to the reservoir, place a clean dry 100-ml calibrated flask below the column outlet, and allow the solution to drain through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary. Dilute the effluent accurately to 100 ml with the 0·2 per cent. v/v solution of acetic acid in methanol and keep this solution for the determination of the 2:6- isomer. Continue the separation, rinse the reservoir with 10 ml of the 5 per cent. v/v solution of acetic acid in methanol, allow the rinsings to drain to waste and leave the capillary stem filled with liquid. Add 95 ml of the 5 per cent. v/v solution of acetic acid in methanol to the reservoir, place a clean dry 100-ml calibrated flask below the outlet tube, and allow the solution to drain through the column at 3 ml per minute; no attention is required and the liquid level may be allowed to drain into the capillary. Dilute the effluent accurately to 100 ml with the 5 per cent. v/v solution of acetic acid in methanol and keep the solution for the determination of 2:4:6-trichlorophenol.

(*a*) *Determination of the* 2:6- *isomer*—Measure the absorption of the effluent obtained with the 0·2 per cent. v/v solution of acetic acid in methanol at 285 mμ in a 1-cm cell, using the 0·2 per cent. v/v solution of acetic acid in methanol as the blank.

Prepare a standard solution of the pure 2:6- isomer at a concentration of 0·005 per cent. w/v (5 mg per 100 ml) in the 0·2 per cent. v/v solution of acetic acid in methanol. Measure the absorption in the same way as for the sample solution.

If the absorptions are A and A', respectively, then the weight of 2:6- isomer from sample $= \frac{A}{A'} \times 5$ mg.

As the total sample weight is 100 mg—

$$2:6\text{- Isomer, per cent.} = \frac{5A}{A'}.$$

(*b*) *Determination of* 2:4:6-*trichlorophenol*—Measure the absorption of the effluent obtained with the 5 per cent. v/v solution of acetic acid in methanol at 296 mμ in a 1-cm cell, using the 5 per cent. v/v solution of acetic acid in methanol as the blank.

Prepare a standard solution of pure 2:4:6-trichlorophenol at a concentration of 0·005 per cent. w/v (5 mg per 100 ml) in the 5 per cent. v/v solution of acetic acid in methanol and measure the absorption in the same way as for the sample solution.

If the absorptions are A and A', respectively, then—

$$2:4:6\text{-trichlorophenol, per cent.} = \frac{5A}{A'}.$$

PROCEDURE FOR DETERMINING *p*-CHLOROPHENOL—

Transfer about 100 to 150 ml of sample solution I to the reservoir of a clean column and fill the capillary by allowing a small amount of the solution to drain to waste. Allow the solution to drain through the column at 3 ml per minute, and collect the effluent in 10-ml fractions and measure the absorptions of the fractions at 283 mμ in 1-cm cells, using the "composite" solution as the blank. The absorptions will rise to a steady value after 4 or 5 fractions.

Prepare a standard solution of pure *p*-chlorophenol at a concentration of 0·005 per cent. w/v (5 mg per 100 ml) in the "composite" solution and measure the absorption at 283 mμ in a 1-cm cell against the same blank.

If the absorption of the standard solution $= P$ and
the steady absorption from sample $= S$,

then the weight of *p*-chlorophenol per 100 ml of sample solution $= \frac{S}{P} \times 5$ mg.

As 100 ml of sample solution contain 100 mg of sample—

$$p\text{-Chlorophenol, per cent.} = \frac{5S.}{P}$$

PROCEDURE FOR REGENERATING THE COLUMNS OF RESIN—

The columns may be used repeatedly if they are regenerated as described in Part I, p. 569.

RESULTS AND DISCUSSION

RESULTS—

A series of commercial samples of 2:4-dichlorophenol was analysed by the proposed methods and the results are shown in Table I.

TABLE I

ANALYSIS OF COMMERCIAL 2:4-DICHLOROPHENOL

Sample No.	Setting point of sample, °C	2:4- Isomer found, %	2:6- Isomer found, %	2:4:6-Trichlorophenol found, %	*p*-Chlorophenol found, %	Total, %
1	40·7	96·6	3·8	<0·1	0·3	100·7
2	40·0	95·6	3·6	<0·1	0·4	99·6
3	38·0	90·9	6·1	2·3	0·4	99·7
4	37·55	91·9	4·9	1·6	0·8	99·2
5	37·0	88·0	5·6	5·6	0·2	99·4

REPRODUCIBILITY—

The reproducibility of the method was examined by replicate analysis performed with two separate columns. The ultra-violet absorptions (*a*) for the 2:4- isomer were: for sample No. 1, 0·745 and 0·744; for No. 2, 0·737 and 0·736; and for No. 3, 0·700 and 0·700: (*b*) for the 2:6- isomer were: for sample No. 1, 0·568 and 0·570; and for No. 2, 0·545 and 0·539.

The precision of measurement with the Unicam SP500 spectrophotometer is quoted as ±0·003. The values obtained in replicate analyses are well within this precision. After allowance has been made for the full instrumental variation for the main component (the 2:4- isomer) when absorptions of about 0·7 are being measured, the precision is greater than ±0·5 per cent.

ACCURACY—

In order to achieve a high accuracy in the determination of the 2:4- isomer, it was essential to prepare a very pure specimen of this material for standard measurements.

A specimen was finally prepared by repeated recrystallisation of the best available commercial 2:4-dichlorophenol (setting point, 40·7° C) from light petroleum, boiling range 40° to 60° C. The mother liquor from each crystallisation was evaporated to dryness to provide the material for the subsequent crystallisation. The melting-point of the final material, after 4 crystallisations, was 44·8° C by the capillary method.

This material was analysed by the methods described, separate columns being used for duplicate analyses.

(*a*) *Determination of the* 2:4- *isomer*—The ultra-violet absorptions for the effluents obtained with the dilute solution of triethylamine acetate in methanol and collected as described under "Procedure for determining the 2:4- isomer," p. 577, were 0·770 and 0·771.

A standard solution of the original material (m.p. 44·8° C) was prepared directly in the dilute solution of triethylamine acetate in methanol at a concentration of 0·005 per cent. w/v (10 mg per 200 ml) and measured directly under the same conditions. The absorption value was 0·772. Therefore, the recovery was 100 per cent. and the specimen was accepted on this basis as having a purity of 100·0 ± 0·5 per cent.

(*b*) *Determination of the* 2:6- *isomer*—A slightly modified technique was employed to determine the 2:6- isomer in the specimen (m.p. 44·8° C). As a very low absorption was expected, increased sensitivity was achieved by collecting the effluent obtained with the 0·2 per cent. v/v solution of acetic acid in methanol in 10-ml fractions and measuring the absorptions of the fractions individually. The absorptions obtained at 285 mμ in 1-cm cells were as follows, the equivalent theoretical absorption for column 1 being 0·196 and that for column 2 being 0·204—

Fraction No.	1	2	3	4	5	6	7 to 10
Absorption (column 1)	0·028	0·093	0·049	0·017	0·009	0·000	0
Absorption (column 2)	0·037	0·099	0·046	0·013	0·005	0·004	0

When the absorptions found were recalculated to a volume of 100 ml the values were 0·0196 and 0·0204, which correspond, respectively, to 0·12 and 0·13 per cent. of the 2:6- isomer.

The method indicated under "Absorption of 2:6-dichlorophenol at pH 8·0," p. 573, was not applied to the specimen, since economy of the sample was important.

There was no evidence of any 2:4:6-trichlorophenol or *p*-chlorophenol being present.

THEORETICAL CONSIDERATIONS—

A brief survey of the theoretical background was carried out in an attempt to provide a criterion for predicting the behaviour of any particular phenol. A suitable criterion is available in the apparent dissociation constants of the phenols as determined by the shift in their ultra-violet absorption spectra with increasing pH.[4] The ultra-violet absorption spectra of a series of chlorophenols were determined in methanol with use of triethylamine - acetic acid buffer solutions of approximate concentrations of 0·2 per cent. v/v. (A small error was introduced in the determination of the maximum absorption value of the ionisation peak, since to ensure complete ionisation this measurement was carried out in aqueous sodium hydroxide.) The percentage of ionisation was calculated and plotted against the pH, and the resulting curves are shown in Fig. 4.

From a study of these curves, the following general observations may be made—

(*a*) *Acid conditions*—When acid solutions are employed for the elutions, the only effect apparently operating is the "natural" selectivity of the anion-exchange resin. Under these conditions the chlorophenols are eluted in the inverse order of their apparent dissociation constants (pK = pH at 50 per cent. ionisation), *viz.*, 2:4-, 3:4:5-, 2:4:5-, 2:4:6- and 2:3:6-.

One exception is noted in 2:6-dichlorophenol, which is eluted together with the 2:4-dichlorophenol in acid solution.

(*b*) *High pH*—In the separation of 2:4- and 2:6-dichlorophenols at pH 8·0 it will be noted that the 2:4-dichlorophenol, which is easily eluted at this pH, is ionised to the extent of only 5 per cent., whereas the 2:6-dichlorophenol, which is strongly retained by the resin, is ionised to the extent of 21 per cent.

A similar state of affairs exists in the separation of 2:4-dichlorophenol and *p*-chlorophenol. (The graph for *p*-chlorophenol is not shown; accurate results could not be obtained with this phenol, since the triethylamine - acetic acid buffer solutions did not cover a high enough range of pH.) The ionisation of 2:4-dichlorophenol at the pH of this separation (8·6) had increased to 12 per cent., whereas the *p*-chlorophenol showed no appreciable ionisation. The 2:4-dichlorophenol was strongly retained, whereas the *p*-chlorophenol was easily eluted. The *p*-chlorophenol ionises appreciably at higher pH values (9·8 with the 0·2 per cent. v/v solution of triethylamine in methanol) and is strongly retained under these conditions.

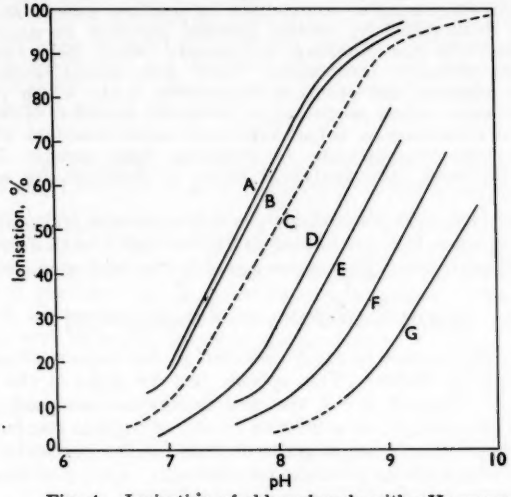

Fig. 4. Ionisation of chlorophenols with pH: curve A, 2:3:6-trichlorophenol; curve B, 2:4:6-trichlorophenol; curve C, theoretical curve (pK 8·0); curve D, 2:4:5-trichlorophenol; curve E, 2:6-dichlorophenyl; curve F, 3:4:5-trichlorophenol; curve G, 2:4-dichlorophenol

In general terms, therefore, it may be stated that the optimum pH for the separation of any pair of phenols is that at which one of the phenols is 5 per cent. or less ionised while the other is ionised to the extent of 12 per cent. or more.

It may be pointed out that this criterion can be applied to phenols in solution without isolating the pure phenol. The pH of the solution may be progressively adjusted and the ultra-violet absorption spectrum determined at suitable pH intervals.

Conclusions

The method described provides a rapid, precise and accurate method for the determination of all the components in commercial 2:4-dichlorophenol. A suitable criterion for the selection of the optimum pH required in the ion-exchange separation of any pair of phenols is provided by a study of the ionisation of the phenol at different pH levels. The technique should be applicable to a wide range of phenols apart from the chlorophenols discussed in this paper.

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The Use of Fusion Reactions with Benzoyl Peroxide in Organic Spot-test Analysis

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Translated by R. E. OESPER†

The following organic compounds, or certain groups in them, are oxidatively decomposed by molten benzoyl peroxide in a characteristic manner: O-methyl and N-methyl compounds, which yield formaldehyde; N-ethyl and propenyl compounds, which give acetaldehyde; aliphatic oximes and aliphatic and aromatic hydroxamic acids, which yield nitrous acid. Since these fission products can be readily detected in the gas phase by means of characteristic colour reactions, fusion reactions with benzoyl peroxide provide new methods of detecting these groups. If spot-test techniques are used, microanalytical limits of detection are achieved.

It was recently shown[1] that dyes possessing *p*-phenylenediamine and *p*-nitroaniline structures are reductively cleaved when they are heated to 210° to 230° C with a dry mixture of sodium formate and sodium hydroxide. The active agent is the hydrogen produced, the reaction being as follows—

$$NaOH + HCOONa \longrightarrow Na_2CO_3 + 2H$$

The resulting *p*-phenylenediamine is easily detected in the vapour phase by the phenylene blue reaction developed by Heim.[2] This specific test for dyes of the cited structure has detection limits of 5 to 10 μg of dye if spot-test techniques are used.

It seemed logical to attempt the oxidative fission of organic compounds in the absence of solvents with the hope of arriving at indirect tests for the particular group through the detection of characteristic gaseous products on cleavage. This goal was reached by fusion with benzoyl peroxide.

Benzoyl peroxide, dissolved in organic liquids, is widely used as an oxidant; it also reacts in solid form. This is shown by the fact that, in intimate mixture with *pp'*-tetramethyldiaminodiphenylmethane (tetra base), it converts the latter into the familiar blue quinoidal oxidation product.[3] This solid - solid reaction, which is the basis of a sensitive test for benzoyl peroxide,[4] made it likely that oxygen would also be released, as follows—

$$(C_6H_5CO)_2O_2 \longrightarrow (C_6H_5CO)_2O + O$$

on contact of this peroxide with other appropriate oxygen acceptors. It is apparent that the maximum contact is attained, together with the greatest readiness to undergo the decomposition shown in the equation, with molten benzoyl peroxide. Since benzoyl peroxide melts at 103° C, or at 110° C when heated rapidly,[5] there is no danger at this temperature of pyrolysis of the organic compounds under test, which might hide the reaction picture. Activity as oxygen acceptors was expected with compounds containing >C=C<, >C=S or >C=N– groups, since in them there is great likelihood of the production of fission materials with terminal >C=O groups.

It was found that when propenyl compounds are fused with benzoyl peroxide they yield acetaldehyde, possibly through the reaction—

$$R\text{–}CH{=}CHCH_3 + 2(C_6H_5CO)_2O_2 \longrightarrow 2(C_6H_5CO)_2O + RCHO + CH_3CHO \ldots \quad (1)$$

Contrary to our expectations, no oxidative cleavage with formation of acetone or formaldehyde could be established when compounds containing $\begin{matrix}CH_3\\CH_3\end{matrix}>C=$ or $-CH=CH_2$ groups were used. Trials were made with citral and methylheptanone, and also with cinchonine and chlorophyll, which contain vinyl groups.

An oxidative cleavage with formation of nitrous acid was found when benzoyl peroxide was fused with aliphatic oximes, and with aliphatic and aromatic hydroxamic acids, which

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contain oxime groups in their tautomeric hydroximic acid form. The reactions may be written—

$$RRC{=}NOH + 2(C_6H_5CO)_2O_2 \longrightarrow 2(C_6H_5CO)_2O + RRCO + HNO_2 \quad .. \quad .. \quad (2)$$

$$RCONHOH \rightleftharpoons RC(OH){=}NOH + 2(C_6H_5CO)_2O_2 \longrightarrow 2(C_6H_5CO)_2O + RCOOH + HNO_2 \quad .. \quad (3)$$

When thioketones are fused with benzoyl peroxide, sulphur dioxide results, obviously through the reaction—

$$>C{=}S + 3(C_6H_5CO)_2O_2 \longrightarrow 3(C_6H_5CO)_2O + >C{=}O + SO_2 \quad .. \quad .. \quad (4)$$

Although an oxidative cleavage is plausible in reactions (1), (2), (3) and (4), in which benzoyl peroxide reacts with compounds containing >C= groups, this is not so for compounds containing $-OCH_3$, $>NCH_3$, $-OC_2H_5$ or $>NC_2H_5$ groups. Surprisingly, it was found that these groups likewise enter into an oxidative cleavage with benzoyl peroxide to yield formaldehyde or acetaldehyde. It seems logical to represent these findings as due to an oxidative cleavage coupled with a migration of hydrogen atoms from CH_3- or C_2H_5- groups to carbon or nitrogen atoms, as the case may be—

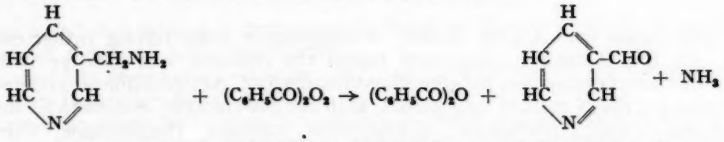
$$R{-}OCH_3 + (C_6H_5CO)_2O_2 \longrightarrow (C_6H_5CO)_2O + ROH + HCHO \quad .. \quad .. \quad (5)$$

$$>NCH_3 + (C_6H_5CO)_2O_2 \longrightarrow (C_6H_5CO)_2O + >NH + HCHO \quad .. \quad .. \quad (6)$$

$$R{-}OC_2H_5 + (C_6H_5CO)_2O_2 \longrightarrow (C_6H_5CO)_2O + ROH + CH_3CHO \quad .. \quad .. \quad (7)$$

$$>NC_2H_5 + (C_6H_5CO)_2O_2 \longrightarrow (C_6H_5CO)_2O + >NH + CH_3CHO \quad .. \quad .. \quad (8)$$

This assumption of an oxidative cleavage accompanied by a migration of hydrogen atoms is admissible if consideration is given to the behaviour of 2-methylaminopyridine and thioglycollic acid when warmed with benzoyl peroxide. Even at 100° C considerable amounts of ammonia and hydrogen sulphide are produced—



$$CH_2(SH)\cdot COOH + (C_6H_5CO)_2O_2 \rightarrow (C_6H_5CO)_2O + CHO\cdot COOH + H_2S$$

Evidence for the correctness of the formulation of the oxidative cleavage of >C= groups as shown in equations (1), (2), (3) and (4) was found in the behaviour of nitroethane. When its mixture with benzoyl peroxide is heated, even to as low a temperature as 100° C, nitrous acid is split off, patently from the tautomeric *aci* form—

$$CH_3CH_2NO_2 \rightleftharpoons CH_3CH{=}NO_2H + (C_6H_5CO)_2O_2 \longrightarrow (C_6H_5CO)_2O + CH_3CHO + HNO_2$$

The oxidative cleavages shown in reactions (1) to (8) cannot be realised, or only partly, in the wet way by warming the participants dissolved in organic liquids. Hence the findings reported here reveal a remarkable and hitherto apparently overlooked reactivity of fused benzoyl peroxide.

Milligram amounts of benzoyl peroxide are sufficient to accomplish the above-mentioned reactions with microgram amounts of the particular reactive compounds. The only exception is ethoxy compounds (see later). The sensitive detection of the resulting aldehyde, nitrous acid or sulphur dioxide in the gas phase accordingly makes possible simple tests for those groups that enter into the oxidative cleavage. Formaldehyde can be detected by a modification of the Eegriwe[6] colour reaction with chromotropic acid.[7] Acetaldehyde is detected by means of the Lewin[8] colour reaction with sodium nitroprusside and piperidine (the piperidine can be replaced advantageously by the cheaper morpholine[9]). The formation of nitrous acid is readily established by the familiar Griess test. The autoxidation of green $Ni(OH)_2$ to black $NiO(OH)_2$, which is induced by sulphur dioxide, can be utilised to detect the latter.[10]

The use of benzoyl peroxide for the detection of oxidatively cleaved compounds has been tested on almost eighty compounds on the spot-test scale. The results were satisfactory with the sole exception of ethoxy compounds. With them, the expected acetaldehyde is evolved only at higher temperatures and hence there is danger of deflagration. Consequently, the procedure cannot be recommended for the detection of ethoxy compounds, but it should be remembered that the spot-test involving wet-oxidation with chromic acid has proved very satisfactory.[11]

In a later paper the findings about the detection of thioketones and also the behaviour of thiol compounds, disulphides and thioethers will be reported. Experiments dealing with the analytical use of fusions with benzoyl peroxide for detecting aliphatic and aromatic nitro compounds in their *aci* form are in progress.

EXPERIMENTAL

Detection of O-methyl and N-methyl compounds

Reagent—

Chromotropic acid - sulphuric acid mixture—Several milligrams of pure chromotropic acid are stirred with 2 ml of concentrated sulphuric acid. The reagent must be freshly prepared.

Procedure—

The test is conducted in the gas-absorption apparatus commonly used in spot-test analysis, when it is desired to have a gas or vapour that has been released to come into contact with a hanging drop of a solvent or a reagent solution A small amount of the solid or liquid sample, or a drop of its solution in benzene, ether or chloroform, is placed in the bulb of the apparatus and then 2 drops of a 10 per cent. solution of benzoyl peroxide in benzene are added. The solvent is evaporated. The apparatus is placed in a glycerol bath that has been heated to between 120° and 130° C. A drop of the chromotropic acid - sulphuric acid reagent solution is placed on the knob of the stopper, which is then put in place. The response is positive if the hanging drop turns violet within several minutes. The colour is quite visible, even with very small amounts of formaldehyde, if the drop is placed on a white spot-plate. It is advisable to carry out a comparison blank test.

Results—

Tests were made with a large variety of compounds, some having rather complicated structures. Of the O-methyl compounds tested the response was positive with anisole, veratrole, *p*-methoxybenzhydrol, *pp'*-dimethoxybenzhydrol, methylcellulose, codeine, brucine and papaverine; of the N-methyl compounds, with choline chloride, *m*-dimethylaminophenol, N-methyldiphenylamine, phenazone, aminopyrine, caffeine, theobromine, theophylline, pilocarpine, methyl orange, methyl red, methyl violet and malachite green.

It was found that 10 μg of methyl orange, 20 μg of aminopyrine, 20 μg of brucine, 40 μg of caffeine, 40 μg of codeine and 100 μg of phenazone could be detected.

The test is not applicable to compounds that themselves yield formaldehyde when heated. It should also be noted that numerous organic compounds, including some that are volatile, give coloured solutions in concentrated sulphuric acid. Therefore, a preliminary trial should be made without the addition of benzoyl peroxide. If a marked coloration of the hanging drop ensues, the procedure is not applicable.

A preliminary separation is necessary in case both O-methyl and N-methyl compounds are present. If an ether solution is presented for testing, it should be shaken with dilute hydrochloric acid. The N-methyl compounds pass into the water layer as hydrochlorides and may be extracted from the aqueous solution by ether after the base has been set free by alkali. The residue on evaporation of the ether solution can then be subjected to the fusion with benzoyl peroxide.

Detection of N-ethyl compounds

Reagent—

Morpholine reagent—A freshly prepared mixture of equal volumes of a 20 per cent. solution of morpholine in water and a 5 per cent. aqueous solution of sodium nitroprusside.

Procedure—

The test is conducted in a micro test-tube. A small amount of the solid, or the residue on evaporation of a drop of the test solution, is treated with 2 drops of a 10 per cent. solution of benzoyl peroxide in benzene, and the mixture is evaporated to dryness on a water bath. The mouth of the test-tube is covered with filter-paper that has been moistened with a drop of the morpholine reagent solution. The tube is hung in a glycerol bath at 120° to 130° C. Depending on the amount of N-ethyl compound present, a more or less intense blue stain appears on the paper within a few minutes.

RESULTS—

A positive response was obtained from mono- and di-ethylaniline, N-ethyl-4-aminocarbazole, brilliant green, ethyl orange, coelestine blue, rhodamine B, procaine hydrochloride, procaine penicillin G, nikethamide (NN-diethylnicotinamide), mepacrine hydrochloride [3-chloro-7-methoxy-9-(1-methyl-4-diethylaminobutylamino)acridine dichloride] and chloroquine phosphate [7-chloro-4-(4-diethylamino-1-methylbutylamino)quinoline diphosphate].

It was found that 15 μg of ethyl orange, 25 μg of brilliant green and 50 μg of rhodamine B could be detected.

DETECTION OF PROPENYL COMPOUNDS

Trials with the propenyl compounds tested showed that the reactions with benzoyl peroxide occur at temperatures as low as 100° C, *i.e.*, close to the melting-point of the peroxide.

REAGENT—

The *morpholine reagent* as above.

PROCEDURE—

A drop of the test solution is placed in a micro test-tube and a drop of 5 per cent. benzoyl peroxide solution in benzene is added. The mouth of the tube is covered with a disc of filter-paper moistened with the morpholine reagent. The test-tube is plunged into boiling water. If propenyl compounds are present, the paper turns blue, the shade depending on the amount present.

Ethanol should not be used as solvent when very small amounts of propenyl compounds are sought, because there is a distinct oxidation of ethanol to acetaldehyde by benzoyl peroxide.

RESULTS—

It was found that 40 μg of *p*-hydroxypropylbenzene, 60 μg of anethole, 60 μg of *iso*eugenol and 100 μg of *iso*safrole could be detected.

No acetaldehyde is produced from safrole or eugenol, which are the allyl compounds isomeric with *iso*safrole and *iso*eugenol.

It should be noted that the rather volatile propenyl compounds just mentioned evolve vapours at water-bath temperature without addition of benzoyl peroxide, and these volatilised portions colour the paper blue. This effect is probably due to the oxidation to acetaldehyde when the vapours come into contact with sodium nitroprusside, which is an oxidant. This behaviour seems to be characteristic for volatile propenyl compounds and can be employed for their detection, if the maximum of sensitivity is not essential.

The test described here may not be used if acetaldehyde or compounds that yield acetaldehyde under the prescribed conditions are present in the sample. The separation from ethyl-substituted nitrogen bases is readily secured by shaking the test substance in benzene, chloroform and so on with dilute hydrochloric acid; the bases then pass into the water solution as chlorides.

DETECTION OF OXIMES AND HYDROXAMIC ACIDS

REAGENT—

Sulphanilic acid - 1-naphthylamine reagent—A freshly prepared mixture of equal volumes of a 1 per cent. solution of sulphanilic acid in 30 per cent. acetic acid and 1 per cent. solution of 1-naphthylamine in 30 per cent. acetic acid.

PROCEDURE—

A micro test-tube is used. A small amount of the solid, or the residue after evaporation of a drop of its solution, or a drop of its solution in ether or benzene, is treated with a drop of 10 per cent. solution of benzoyl peroxide in benzene and evaporated to dryness. The mouth of the test-tube is covered with a disc of filter-paper moistened with the sulphanilic acid - 1-naphthylamine reagent and the tube is immersed in a glycerol bath previously heated to 120° to 130° C. If aliphatic oximes or aliphatic and aromatic hydroxamic acids are present, a pink or red stain appears within 3 to 10 minutes.

RESULTS—

It was found that 10 μg of dimethylgloxime, 20 μg of *cyclo*heptanedione dioxime and 40 μg of camphor oxime could be detected. A positive response was observed with phenylglyoxaldoxine, furfuraldoxime, butane-2 : 3-dione dioxime and *cyclo*hexane-1 : 2-dione dioxime.

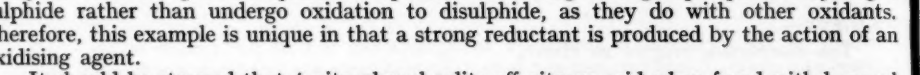
No reaction was given by diphenylglyoxime, salicylaldoxime, benzil α-monoxime, benzil α-dioxime and benzoin α-oxime.

Identification limits of 30 to 40 μg were obtained with benzohydroxamic acid, salicylhydroxamic acid, phenylacetohydroxamic acid and *p*-methoxybenzohydroxamic acid.

Conclusions

It may be fundamental to the oxidative cleavages accomplished by molten benzoyl peroxide that the latter yields particularly active oxygen in the complete absence of water. Consequently, the volatile compounds produced rapidly at the reaction temperature, such as formaldehyde, acetaldehyde, nitrous acid and hydrogen sulphide, are not subjected to further action by benzoyl peroxide. The peculiar action of the latter is shown most impressively in the finding that aliphatic compounds containing –SH groups split off hydrogen sulphide rather than undergo oxidation to disulphide, as they do with other oxidants. Therefore, this example is unique in that a strong reductant is produced by the action of an oxidising agent.

It should be stressed that *p*-nitrophenol splits off nitrous acid when fused with benzoyl peroxide. Accordingly, in the absence of water and hydroxyl ions, this nitro compound reacts in its *aci* (nitronic acid) form—



Since *p*-nitroaniline and dipicrylamine and also (as pointed out before) nitroethane react analogously, it may be predicted with safety that it will be possible to work out a new test for *aci*-nitro compounds.

The tests described under equations (1), (2), (3) and (4) suggest the use of oxidative cleavages with benzoyl peroxide for preparative purposes. Several experiments along this line were not encouraging, because it was impossible to avoid deflagration of benzoyl peroxide with centigram amounts. However, careful manipulation of the fusion reaction with microgram amounts seldom led to explosions, and even then the positive response to the test for acetaldehyde and nitrous acid was undeniable. This demonstrates once more that spot-test analysis can make use of organic reactions that are completely without interest from the standpoint of preparative chemistry.[12]

Although the production of acetaldehyde is not specific, identity tests, for which hitherto there have been no chemical procedures, can nevertheless be based on it. In this connection the reliable differentiation of propenyl from the isomeric alkyl compounds, the distinguishing of N-methyl and N-ethyl compounds from each other and also the detection of such compounds in mixtures should be noted. Hence, it is possible to characterise very similar compounds in mixtures such as: methyl orange and ethyl orange; malachite green and brilliant green; gallamine blue and coelestine blue. The differentiation of these pairs of dyes through their N-methyl and N-ethyl groups, respectively, can be successfully accomplished with even fragments of dyed goods.

Mrs. Cecile Stark-Mayer and Mr. Claudio Costa Neto made numerous careful tests of various compounds during the course of this study. Our thanks are likewise extended to the Conselho Nacional de Pesquisas for its financial support.

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The Determination of Ethylene Oxide in the Atmosphere

By J. C. GAGE

A sensitive colorimetric method is described for the determination of ethylene oxide in the atmosphere. It is based on the separation of ethylene oxide from the sample by means of silica gel, and then oxidation with periodic acid and a colorimetric determination of the formaldehyde produced. The method has been checked on atmospheres of known ethylene oxide content.

PUBLISHED methods for the determination of ethylene oxide in the atmosphere[1,2,3,4] are based on the reaction of the epoxide ring with anions, and then the measurement of the resulting decrease in acid concentration or liberation of alkali. Such a method is subject to inference from acid or alkaline substances that may be present in the atmosphere, and at a recommended maximum allowable concentration of 10 p.p.m.[2] the volume of the air sample must be at least 300 litres in order to obtain a decrease in acidity that can conveniently be measured by titration. Moreover, it is pointed out in one method[2] that in order to obtain efficient absorption two bubblers in series are necessary and these must be maintained at a temperature below 7° C.

Recently, a method for the determination of epichlorhydrin has been described,[5] in which formaldehyde, liberated by oxidation with periodic acid, is measured colorimetrically, and it is noted that this procedure can also be used for ethylene oxide. The absorption of ethylene oxide in water is, however, very inefficient, and in the proposed method the procedure for epichlorhydrin has been modified by passing the air sample through silica gel in order to absorb the ethylene oxide.

METHOD

PREPARATION OF THE ABSORPTION TUBE CONTAINING SILICA GEL—

Select a piece of glass tubing having an internal diameter of 6 mm and about 180 mm long. About 40 mm from one end make a series of indentations around the tube to retain a small plug of cotton-wool. Introduce into the tube 2 g of silica gel of 40 to 60 mesh; the quality supplied by Silica Gel Ltd. has been found suitable for this purpose without further treatment, but it should be kept in a closed container and not exposed to moist or contaminated air. Then put another small plug of cotton-wool in the tube to keep the column of silica gel in position, and close the tube at each end with rubber stoppers or caps until required.

COLLECTION OF AIR SAMPLE—

Connect the prepared tube of silica gel to a water aspirator or other suitable suction device, and draw a sample of the air to be analysed through the tube at a rate of about 0·5 litre per minute. The volume of air sample taken should not contain more than 40 μg of ethylene oxide.

REAGENTS—

Periodic acid solution, 0·2 M—Dissolve 3·84 g of periodic acid in distilled water and dilute to 100 ml.

Sodium arsenite solution, 0·5 M—Dissolve 6·5 g of sodium arsenite in distilled water and dilute to 100 ml.

Acetylacetone reagent—Dissolve 25 g of ammonium acetate, 3 ml of glacial acetic acid and 0·2 ml of redistilled acetylacetone in distilled water and dilute to 100 ml.

Standard ethylene oxide solution—Weigh a stoppered glass flask containing about 20 ml of distilled water, add a few millilitres of liquid ethylene oxide, and weigh again. Dilute the solution so that—

1 ml ≡ 10 μg of ethylene oxide.

Standard potassium chromate solution—Dissolve 125 mg of potassium chromate in water and dilute to 100 ml.

1 ml ≡ 10 μg of ethylene oxide.

In the preparation of these solutions reagents of recognised analytical grade should be used when available. All the solutions, with the exception of the standard ethylene oxide solution, which should be prepared freshly, are stable for at least 1 month.

PROCEDURE FOR DEVELOPING COLOUR—

After the air sample has been passed through the tube containing silica gel, tip the contents of the tube into 10 ml of water in a glass-stoppered test-tube. Add 1 ml of 0·2 *M* periodic acid solution and heat the test-tube in a boiling-water bath for 40 minutes. Add 2 ml of 0·5 *M* sodium arsenite solution and then 2 ml of acetylacetone reagent. Replace the stopper and heat for 3 minutes. Decant the clear liquid from the silica gel and filter if turbid; this is the test solution.

PROCEDURE FOR MEASURING COLOUR—

The determination of the ethylene oxide content of the air sample by means of a visual comparison of the test solution with chromate standards, or by an instrumental colour measurement with reference to a previously prepared standard curve, is performed in a manner similar to that described for epichlorhydrin.[5] For the preparation of the standard curve, 1·0, 2·0, 3·0, 4·0 and 5·0-ml portions of the standard ethylene oxide solution are diluted to 10 ml, 2 g of silica gel are added, and the operation described under "Procedure for Developing Colour" is completed. The optical densities developed are measured in a suitable absorptiometer at 412 mμ, with the colour developed in a similar manner from 10 ml of water as a reagent blank. The optical density of the test solution is applied to this standard curve and the equivalent volume of standard ethylene oxide solution is determined, the reagent blank being taken into consideration. If V is the volume of air sampled, and Y is the volume in ml of standard ethylene oxide solution or standard chromate solution equivalent to the test solution, then the ethylene oxide content of the atmosphere expressed in mg per cubic metre is given by the expression $10\ Y/V$, and the concentration in parts per million (v/v) is given by the expression $0{\cdot}55\ Y/V$.

TABLE I

RESULTS ON TEST ATMOSPHERES

Concentration of ethylene oxide		
Expected, mg per cubic metre	Found, mg per cubic metre	Recovery, %
5·6	4·8	85·8
11·2	11·2	100·0
22·4	23·6	105·0
51·5	58·0	112·7
68·5	61·0	89·0
137	137	100·0

RESULTS

Known test atmospheres of ethylene oxide were prepared by the standard method in use in this laboratory,[6] an aqueous solution of ethylene oxide freshly prepared as described above being used. Samples of these atmospheres were collected through tubes of silica gel and analysed as described above. The measurements obtained in these experiments are shown in Table I.

DISCUSSION

The method described for the determination of ethylene oxide in air is much more sensitive than other methods appearing in the literature, and has the advantage of requiring a colorimetric technique and not a titration. The determination will be not subject to interference by traces of acids or alkalis in the atmosphere, but formaldehyde, or substances that can produce formaldehyde under the conditions of the treatment of the solution, may give a positive reaction.

The standard curve obtained by the method described shows a linear relationship between optical density and concentration. The slope of this line is about four-fifths that of a standard curve constructed from solutions to which silica gel has not been added. An allowance for the reduction of colour intensity by silica gel has been taken into consideration in defining the ethylene oxide equivalent of the standard chromate solution.

When the optical density of the colour developed from the standard ethylene oxide solution is applied to a formaldehyde standard curve, it can be deduced that one molecule of ethylene oxide is oxidised by periodic acid to approximately one molecule of formaldehyde. Ethylene glycol subjected to the same oxidation procedure behaves in a similar manner, and it is possible, therefore, to replace the standard ethylene oxide solution by standard solutions of formaldehyde or ethylene glycol.

Technical assistance in this investigation was provided by Mr. Z. S. Berczy.

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March 4th, 1957

The Separation of Sarcosine from Methylaminediacetic Acid

By D. C. Cullum

A method is described for the separation of sarcosine from methylaminediacetic acid by removal of the dibasic acid on an anion-exchange resin.

One of the methods currently in use for the synthesis of sarcosine (N-methylglycine or methylaminemonoacetic acid) is the condensation of methylamine with sodium monochloroacetate in the presence of excess of alkali—

$$CH_3NH_2 + ClCH_2COONa + NaOH \rightarrow CH_3NHCH_2COONa + NaCl + H_2O.$$

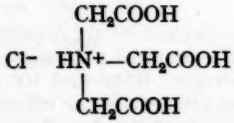
The sodium sarcosinate so formed is able to react with a second molecule of sodium monochloroacetate to produce the sodium salt of methylaminediacetic acid (methyliminodiacetic acid)—

$$CH_3NHCH_2COONa + ClCH_2COONa + NaOH \rightarrow CH_3N(CH_2COONa)_2 + NaCl + H_2O.$$

The formation of the dibasic acid is reduced, but not eliminated, by the use of a large excess of methylamine, which is afterwards removed by distillation. Commercial sarcosine prepared in this way therefore contains methylamine and methylaminediacetic acid. It was believed until recently that a second consecutive reaction occurred between sodium methylaminediacetate and monochloroacetate, resulting in the formation of the sodium salt of methylammonium chloride triacetic acid—

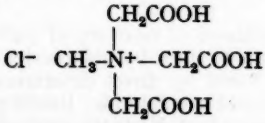
$$CH_3N(CH_2COONa)_2 + ClCH_2COONa \rightarrow CH_3N^+(CH_2COONa)_3Cl^-.$$

However, according to Rodd,[1] ammonia triacetic acid (nitrilotriacetic acid) is unable to form salts such as **I**. It seems highly improbable therefore that compound **II** exists.



(I)

ammonium chloride triacetic acid



(II)

methylammonium chloride triacetic acid

Experiments carried out in this laboratory with methylaminediacetic acid and monochloroacetic acid in excess of alkali have shown that under the conditions of the sarcosine synthesis, at any rate, no such quaternisation occurs.

The method described for the removal of methylaminediacetic acid from solutions of sarcosine depends on the principle used by many workers[2,3,4,5,6,7,8,9,10] in separating glutamic and aspartic acids from monobasic amino acids, *viz.*, the fact that acidic or dibasic amino acids are removed from solution by weakly basic anion-exchange resins in the chloride form, whereas the neutral or monobasic acids are affected only slightly or not at all. Tiselius, Drake and Hagdahl[11] showed that this type of separation could be carried out most conveniently on a column. Hence, when a solution of commercial sarcosine, previously rendered free from methylamine, is passed through a column of De-Acidite E (chloride form), any methylaminediacetic acid present as an impurity is retained by the resin and the sarcosine emerges quantitatively in the effluent. The amount can then be calculated from its nitrogen content found by a standard method.

Method

Apparatus—

Chromatographic column, 400 mm × 18 mm, provided with a stopcock at its lower end and a solvent reservoir at its upper end. In this laboratory apparatus with standard cones and sockets is used.

Prepare in the column an air-free bed of De-Acidite E about 300 mm deep. Before use wash with at least six cycles of *N* sodium hydroxide, water, *N* hydrochloric acid and water, using 250 ml of each liquid. Then wash with water until the concentration of acid in the effluent is less than 0·01 *N*. When the column is in use, the top of the resin bed should be protected by a small pad of clean cotton-wool.

Procedure—

Take a sample of sarcosine solution containing 2 to 2·5 g of the sodium salt or its equivalent. Place it in a 250-ml conical flask and add 100 ml of water and a drop of phenolphthalein solution. If the solution is not alkaline, add sufficient *N* sodium hydroxide to make it so. Then put in two or three glass beads, close the mouth of the flask with a small filter-funnel and boil for 15 minutes to expel any methylamine. Cool the solution, transfer it quantitatively to a 100-ml calibrated flask and dilute to the mark with water.

Allow the water level in the chromatographic column to fall as far as the top of the resin, taking care to admit no air bubbles. By pipette, put 20 ml of the prepared sarcosine solution into the top of the column, allowing it to percolate into the resin at a rate of 4 ml per minute. Reject the effluent. When the liquid level reaches the top of the resin, rinse the walls of the column with about 20 ml of water. This is most easily done by using a pipette. Allow the washings to percolate into the resin at the same rate, collecting the effluent. When the liquid level again reaches the top of the resin, fill the column with water, attach the solvent reservoir, also full of water, and continue to collect the effluent until 120 ml have been collected. This 120 ml contains all the sarcosine, free from other nitrogenous matter. It is essential to avoid exceeding a flow rate of 4 ml per minute, or 1·6 ml per minute per sq. cm if a column of different diameter is used.

Regeneration of the resin—

After each analysis, wash the column with 250 ml of *N* sodium chloride in 0·02 *N* hydrochloric acid, followed by 250 ml of water. After 10 analyses it is advisable to clean the resin with one alkali - water - acid - water cycle as in the preparation of the bed.

Preliminary experiments indicate that De-Acidite G may be as satisfactory as De-Acidite E for this separation.

Results

The completeness of recovery of pure sarcosine was checked by six experiments carried out in two groups of three by independent operators. The material used was pure sarcosine hydrochloride (found by direct determination of the nitrogen: 99·95 and 100·07 per cent. by determination of the chloride: 100·00 per cent.). The nitrogen in the effluent was determined by the standard Kjeldahl method, 5 g of sodium sulphate, 1 g of copper sulphate and 15 ml of sulphuric acid being used for the digestion. The reaction was complete within a few seconds of the commencement of the fuming, and the solution was heated for a further 5 minutes. The following results were obtained for the recovery of sarcosine hydrochlorides—

Operator 1: 100·2, 100·1 and 100·0 per cent.
Operator 2: 100·1, 100·2 and 100·1 per cent.

These indicated satisfactory precision, but further analyses were made in order to show that the sarcosine could be quantitatively recovered when relatively large concentrations of methylaminediacetic acid were initially present. Three mixtures were prepared containing sarcosine hydrochloride and methylaminediacetic acid in the proportions 1 to 1, 2 to 1 and 4 to 1, and were analysed by the proposed method. After the sarcosine had been washed out of the column, the resin was in each test washed with three 100-ml portions of *N* sodium chloride in 0·02 *N* hydrochloric acid, the rate of flow being 4 ml per minute, and the three fractions were analysed separately for nitrogen. The methylaminediacetic acid was found to be quantitatively eluted, at least 95 per cent. of it in the first two fractions. The results are shown in Table I.

TABLE I

RECOVERIES OF SARCOSINE HYDROCHLORIDE AND METHYLAMINEDIACETIC ACID

Sarcosine hydrochloride taken, g	Methylamine-diacetic acid taken, g	Sarcosine hydrochloride found, g	Methylamine-diacetic acid found, g	Recovery of sarcosine hydrochloride, %	Recovery of methylamine-diacetic acid, %
0·4012	0·3858	0·4027	0·3866	100·3	100·3
0·4012	0·3858	0·4020	0·3854	100·2	100·1
0·5984	0·2906	0·5974	0·2943	99·8	101·0
0·5984	0·2906	0·5974	0·2923	99·8	100·6
0·5984	0·2906	0·5969	0·2929	99·7	100·8
0·5984	0·2906	0·5970	0·2943	99·8	101·0
0·4994	0·1269	0·5008	0·1276	100·3	100·6
0·4994	0·1269	0·5016	0·1293	100·4	102·0
0·4994	0·1269	0·5008	0·1276	100·3	100·6

The methylaminediacetic acid used in these experiments was made as described by Blatt.[12] It was found to contain 95·4 per cent. of methylaminediacetic acid by titration with standard alkali, with methyl red as indicator, and 0·62 per cent. of sarcosine (≡ 0·88 per cent. of sarcosine hydrochloride) by the proposed method, the remainder being inorganic matter. The figures for sarcosine hydrochloride in the first column of Table I include this 0·88 per cent.

I thank Mr. J. M. Blakeway and Mr. J. Taylor, of the Research Department, Colgate-Palmolive Ltd., for synthesising the amino acids used in this work, and the management of the Company for permission to publish this paper.

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April 30th, 1957

Notes

THE SEPARATION OF URANIUM FROM LARGE AMOUNTS OF IRON AND ALUMINIUM BY ANION EXCHANGE IN NITRATE MEDIA

THE strong adsorption of chloride complexes of uranyl uranium on anion-exchange resins from hydrochloric acid solutions[1] may be used to separate uranium before its determination. Under such conditions, however, ferric iron is firmly held on the resin[2] and, although reduction to the ferrous state greatly reduces the extent of the uptake of iron, it has been found in practice that it is difficult to maintain iron in the ferrous state at the concentrations of hydrochloric acid necessary for efficient removal of uranium (preferably 6 *M* or greater).

It is known from the work of Kraus and Nelson[3] that uranium is weakly adsorbed on anion-exchange resins from nitric acid solutions. We have found that, with the strongly basic anion-exchange resin De-Acidite FF, the distribution coefficient, *K* (ratio of concentration of ion in the resin phase to that in the aqueous phase), for uranyl uranium reaches a maximum value of about 10 in 7 to 8 *M* nitric acid. This value is too small to effect a clean separation of uranium by the normal column method.

If the nitric acid is replaced by solutions of inorganic nitrates, the distribution coefficient is markedly increased. The effect has been demonstrated with lithium and calcium nitrates,[4] but it is most pronounced with aluminium nitrate, as shown in Fig. 1. Hence, analytical separations of uranium from nitrate solutions become practicable and, although by the batch equilibration procedure equilibrium is only slowly attained, by the column method complete adsorption of uranium is readily achieved. Further, ferric iron is not adsorbed.

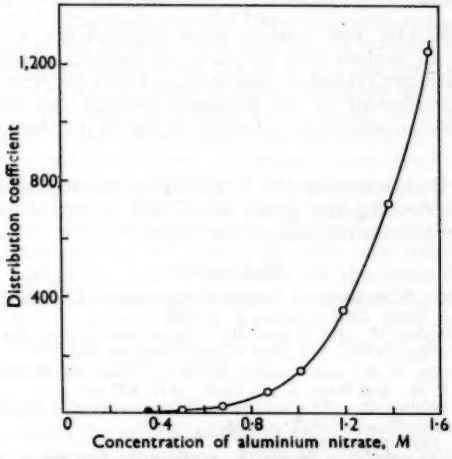

Fig. 1. Distribution coefficient of uranium between De-Acidite FF and aluminium nitrate solution at approximately pH 2

The conditions mentioned above have proved valuable in the separation of both milligram and microgram amounts of uranium from large amounts of iron and aluminium. The procedure is as follows—

Make the sample 0·3 *M* in nitric acid and 1·6 *M* in aluminium nitrate and pass it down a column containing 1·5 g of De-Acidite FF (0·2 to 0·3-mm mesh) previously conditioned to the nitrate form. Wash the column with 6 ml of 1·6 *M* aluminium nitrate solution to remove iron, and then add 8 ml of 8 *M* hydrochloric acid to clear the column of aluminium; the uranium remains on the resin. Elute the uranium with 25 ml of 0·1 *M* hydrochloric acid.

Depending upon the amount of uranium in the eluate, it may be directly determined absorptiometrically by either the alkaline peroxide method[5] (for milligram amounts) or the uranium^{IV}-thoronol method[6] (for microgram amounts).

As both anionic nitrate and chloride complexing occurs with relatively few metals under these conditions, the separation described also gives appreciable decontamination from fission products, the final eluate containing less than 1 per cent. of the original fission-product radioactivity.

This Note is published by permission of the Managing Director, United Kingdom Atomic Energy Authority, Industrial Group.

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THE DETERMINATION OF CERIUM IN BISMUTH-BASE ALLOYS

The usual procedures for the determination of cerium involve titration with ferrous ammonium sulphate after oxidation to the ceric state.[1] In the presence of bismuth, however, difficulties occur in these procedures, especially for high bismuth to cerium ratios. The conditions for the persulphate - silver nitrate method of oxidation allow the presence of only a limited amount of bismuth, owing to the formation of a precipitate that prevents satisfactory boiling of the solution to decompose excess of persulphate. The bismuthate method is reasonably satisfactory for the determination of about 50 mg or greater amounts of cerium in the presence of bismuth, but less satisfactory for approximately 5 mg or less. The preliminary separation of bismuth is necessary for the successful application of these procedures in alloy analysis.

Marple, Przybylowicz and Hume[2] recently described a new approach to the determination of cerium. In their method cerium^{III} is oxidised to cerium^{IV} in potassium pyrophosphate solutions in the pH range 5·5 to 7·0 by direct titration with potassium permanganate. The end-point of the titration is determined photometrically by making use of the increase in absorbancy due to the excess of permanganate in solution after the end-point. Although the behaviour of several elements in this titration is reported, no information is given on the behaviour of bismuth and uranium. Preliminary experiments were therefore undertaken to investigate the behaviour of these constituents in the determination of small amounts of cerium, an E.E.L. absorptiometer (Evans Electroselenium Ltd.) being used for absorption measurements. Ratios of bismuth and uranium to cerium were chosen to comply with values expected to be present in alloy samples. Negligible interference was obtained from these elements, as shown by the results in Table I.

Table I

Effect of bismuth and uranium on the titration of cerium

Cerium taken, mg	Bismuth added, mg	Uranium added, mg	Cerium found, mg	Error, mg
5·05	—	—	5·05	0·00
5·05	200	—	5·07	+0·02
5·05	—	20	5·05	0·00
5·05	200	20	5·07	+0·02
1·01	250	20	1·04	+0·03

As a result of the negligible interference of bismuth and uranium, the following method was developed for the cerium content of bismuth-base alloys.

Method

Apparatus—

E.E.L. absorptiometer with the cell carriage removed to take a 250-ml squat beaker for the titration.

REAGENTS—

Potassium permanganate, 0·005 M—Prepare this solution from analytical-reagent grade solid and standardise it against sodium oxalate. This solution is 0·02 *N* for the cerium titration.

Potassium pyrophosphate solution—Prepare an approximately 11 per cent. w/v solution from the pure salt and filter before use.

PROCEDURE—

Dissolve a weighed amount of the alloy in dilute nitric acid and remove most of the excess of acid by evaporation of the solution to a small volume. Then dilute with water, add 3 to 4 ml of saturated sulphur dioxide solution and boil the solution to expel the excess of this reagent. Cool, transfer to a suitable calibrated flask and dilute to the mark with distilled water. Take an aliquot of not more than 20 ml containing 200 to 300 mg of bismuth and transfer it to a 250-ml squat beaker, add 100 ml of the potassium pyrophosphate solution and adjust to pH 5·5 to 7·0, using a pH meter with a glass electrode system, by the dropwise addition of dilute nitric acid. Place the beaker in position in the E.E.L. absorptiometer and adjust the stirrer so that it does not interfere with the passage of light through the solution. Stir the solution, select the Ilford No. 605 light filters and adjust the light intensity until the meter reads zero on the optical-density scale. Add increments of potassium permanganate solution and take optical-density readings after each addition, allowing time for the needle to settle. Continue the incremental addition of the potassium permanganate solution well past the end-point. Plot a graph of optical density against volume of potassium permanganate added and draw the straight lines through the points before and after the end-point. Read off the end-point from the intersection of the two straight lines.

RESULTS

The procedure described above has been tested on artificial alloy solutions prepared by combining aliquots of standard cerium and uranium solutions with solutions of bismuth in nitric acid. The cerium solution was prepared by dissolving pure cerium metal in dilute hydrochloric acid and then standardised gravimetrically by oxalate precipitation and ignition to cerium oxide, CeO_2. The uranium solution was made by dissolving freshly ignited Specpure U_3O_8 in nitric acid and diluting to volume.

Results for the analysis of artificial alloy solutions covering the range from about 1 to 5 per cent. for both cerium and uranium are given in Table II. Separate aliquots of sample solution were taken for the cerium and uranium determinations. For uranium, the method used involved, precipitation as uranyl ammonium phosphate in the presence of ethylenediaminetetra-acetic acid,[3] after the removal of the bulk of the bismuth as its volatile bromide. The separated precipitate was dissolved in hydrochloric acid and the uranium was reduced to the quadrivalent state by passage through a lead reductor before titration with standard ceric sulphate solution. The results in Table II confirm the suitability of the procedure for the determination of these constituents.

TABLE II

RESULTS FOR ARTIFICIAL BISMUTH - URANIUM - CERIUM ALLOYS

Cerium in alloy, %	Cerium found by analysis, %		Uranium in alloy, %	Uranium found by analysis, %	
1·01	1·00	1·00	4·72	4·71	4·72
2·06	2·10	2·11	1·92	1·90	1·90
4·67	4·64	4·64	0·94	0·94	0·94

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ANALYTICAL CHEMISTRY GROUP
ATOMIC ENERGY RESEARCH ESTABLISHMENT
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April 17th, 1957

THE NEPHELOMETRIC DETERMINATION OF ARSENIC

THE proposed method is based on the reduction of arsenic to the colloidal metallic state with hypophosphite. The precipitation of metallic arsenic by hypophosphorous acid has been described by Thiele.[1] This precipitation has been used as a means of separation subsequent to titration procedures for the determination of arsenic.[2,3,4]

Under controlled conditions this colloidal metallic arsenic should be measurable nephelometrically, and in this Note a method is described for this measurement, particularly in its application to arsenical copper and other copper-base alloys.

METHOD

REAGENTS—

All reagents should be of recognised analytical grade.

Ammonium persulphate, saturated solution.

Sulphuric acid, diluted—Containing approximately 400 g per litre.

Nitric acid, concentrated.

Bougault reagent—Dissolve 20 g of sodium hypophosphite in 20 ml of distilled water, add 200 ml of concentrated hydrochloric acid and filter off the sodium chloride. Store the solution in a cool place and re-filter it after 1 week; keep it in a brown glass bottle.

Potassium permanganate solution, 10 g per litre.

Standard arsenic solution—Dissolve 0·500 g of sodium hydroxide in distilled water, add 0·1000 g of arsenious oxide and, when dissolved, dilute to 1 litre.

PROCEDURE—

Weigh 0·5000 g of sample (copper or copper alloy) into a 250-ml conical beaker and dissolve it in 25 ml of diluted sulphuric acid and 3 to 4 ml of nitric acid. Cover the beaker with a watch-glass and heat until solution is complete and brown fumes of nitrous oxide are expelled. Then add 2 ml of potassium permanganate solution and boil until the manganese dioxide is completely precipitated. Add 1 to 2 ml of ammonium persulphate solution and boil until the solution is clear. Wash down the watch-glass and sides of the beaker with a small amount of water. Heat to copious fumes and continue to heat for 5 minutes or more. Allow the beaker to cool, add water and dilute the contents to 100 ml in a calibrated flask.

By pipette put a 10-ml aliquot into a 1-inch tube and add 10 ml of the Bougault reagent. Place the tube in a water bath that is boiling before insertion of the tubes and heat it for 30 minutes. Remove the tube from the boiling water and allow it to cool in the air. Adjust the volume to 20 ml with 9 *N* hydrochloric acid. Measure the optical density of the dispersed colloid in a colorimeter or spectrophotometer.

PREPARATION OF CALIBRATION GRAPHS—

Weigh 0·5000-g portions of high-conductivity copper into nine 250-ml conical beakers. Add standard arsenic solution to give 0·05, 0·10, 0·20, 0·30, 0·40, 0·50, 0·60 and 0·75 per cent. of arsenic for establishing the calibration graph. Prepare one sample without arsenic as a blank. To each beaker add 25 ml of diluted sulphuric acid and 3 to 4 ml of nitric acid and continue as under "Procedure."

If the optical densities of the solutions are measured with a Beckman model B spectrophotometer or an Evelyn colorimeter, 1-cm cells or 1-cm tubes, respectively, should be used. The maximum apparent absorbance was found to be at 6120 A with the Beckman model B spectrophotometer and readings with this instrument were made at this wavelength. A No. 600 orange filter was used for readings taken with the Evelyn colorimeter.

RESULTS

For comparative purposes the arsenic content of some arsenical copper billets was determined by different methods. Some of the results are shown in Table I. In the gravimetric method the arsenic was precipitated as arsenic pentasulphide and ultimately weighed as such. For the volumetric determination the precipitated arsenic pentasulphide was dissolved in acid and this solution was titrated with standard iodine solution. The distillation method involved the reduction of the arsenic to arsenic trichloride, which was distilled off and subsequently titrated with standard iodine solution. The colorimetric method (molybdenum blue) involved the determination of arsenic together with phosphorus, stannous chloride being used for reduction. The phosphorus

was determined separately as the molybdovanadophosphate complex and the arsenic was calculated by difference. The nephelometric method is the one described in this Note.

Phosphorus has no effect on the nephelometric determination of arsenic. This is evident from the large amount of hypophosphorous acid (Bougault reagent) used in the method and from Table II, where phosphate was added as an impurity, and also by comparison of the phosphorus content with that of arsenic as is shown in Table I.

TABLE I

COMPARISON OF DIFFERENT METHODS FOR DETERMINING ARSENIC IN ARSENICAL COPPER BILLETS

Phosphorus in billets found by—		Arsenic in billets found by—				
Colorimetric (molybdo-vanado-phosphate) method, %	Gravimetric ($Mg_2P_2O_7$) method, %	Gravimetric (As_2S_3) method, %	Volumetric (iodine titration) method, %	Distillation ($AsCl_3$) method, %	Colorimetric (molyb-denum blue) method, %	Nephelo-metric method, %
0·000	0·000	0·010	0·009	0·010	0·011	0·010
0·010	0·010	0·163	0·166	0·162	0·180	0·164
0·070	0·070	0·298	0·304	0·300	0·290	0·298
0·026	0·026	0·320	0·320	0·322	0·360	0·321
0·035	0·035	0·396	0·400	0·400	0·371	0·396
0·050	0·049	0·435	0·435	0·431	0·464	0·435
0·076	0·078	0·480	0·474	0·469	0·422	0·477
0·031	0·030	0·490	0·498	0·496	0·546	0·494

EFFECT OF VARIATIONS IN PROCEDURE

Prepared solutions of high-conductivity copper with 0·350 per cent. of arsenic added were tested to determine the effect of various experimental conditions.

Fuming time—It is essential that all trace of nitrates be removed by heating to copious fumes; evaporating to dryness did not affect the determination of arsenic.

Permanganate additions—At least 2 ml of permanganate solution are required and additions of 20 ml had no deleterious effect. Sufficient persulphate must be added to dissolve any precipitated manganese dioxide.

Water-bath temperature—The water-bath temperature is important. Calibration is made at 100° C and any lowering of temperature gives low results, *e.g.*, when the water-bath temperature was 90° C, 0·34 per cent. of arsenic was found and when 80° C, 0·29 per cent.

Boiling time—Boiling time has, as might be expected, considerable influence on the colloidal state and it was found that boiling for 30 minutes $\pm$ 1 minute gave consistent results.

The loss by evaporation when the sample is boiled for 30 minutes in the water bath reduces the volume from 20 ml to about 17 ml. For routine work adjustment of the volume may be dispensed with if the calibration graph is prepared under similar conditions. Otherwise the volume should be adjusted to 20 ml with 9 *N* hydrochloric acid for both the preparation of the calibration graph and the test sample.

Cooling conditions—Samples were cooled (*a*) in running water, (*b*) at room temperature and (*c*) in a water bath. Cooling at room temperature gave results in agreement with the known arsenic content. For example, 0·345 per cent. of arsenic was found after cooling in running water, 0·350 per cent. after cooling at room temperature and 0·362 per cent. after cooling in a water bath.

Presence of impurities—A series of determinations was carried out on portions of the prepared solution to which had been added 0·5 per cent. of impurities. The results were as follows—

Impurity added ..	Tin	Nickel	Lead	Iron	Manganese	Phosphate
Arsenic found, % ..	0·348	0·350	0·350	0·352	0·352	0·350
Impurity added ..	Silicon	Bismuth	Aluminium	Nitrate	Chloride	
Arsenic found, % ..	0·355	0·359	0·351	0·062	0·350	

STABILITY OF THE COLLOID—

The colloidal arsenic produced by the method is stable for at least 8 hours when the arsenic content is 0·5 per cent. or less. The stability of the colloid is shown by the results in Table II

TABLE II

STABILITY OF COLLOIDAL ARSENIC

Arsenic added, %	Arsenic found after— ½ hour, %	1 hour, %	2 hours, %	8 hours, %	24 hours, %	240 hours, %
0·10	0·10	0·10	0·10	0·10	0·10	0·10
0·20	0·20	0·20	0·20	0·20	0·20	0·18
0·30	0·30	0·30	0·30	0·30	0·29	0·26
0·40	0·40	0·40	0·40	0·40	0·39	0·32
0·50	0·50	0·50	0·50	0·50	0·47	0·40
0·60	0·60	0·60	0·60	0·56	0·42	*
0·70	0·70	0·70	0·70	*	*	*
0·80	0·80	0·80	0·80	*	*	*
0·90	0·90	0·90	*	*	*	*
1·00	1·00	*	*	*	*	*

* Indicates coagulation of the colloid.

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October 15th, 1956

THE DETERMINATION OF INDOLE IN TAR FRACTIONS

To enlarge the scope of a research project on the assay of coal tars, it was found necessary to survey methods for the determination of certain of the minor constituents of the tars, including indole.

Ehrlich's reagent (*p*-dimethylaminobenzaldehyde) has been used to determine indole in biological materials,[1,2] but, since it would be expected to give coloured reaction products with other components of tar, its use in a possible method was rejected. The method of Karavaev and Venier,[3] for the determination of indole in tar oils, is based on extraction with water, followed by reaction with nitrous acid to produce a red colour. This method was found to be limited by the insolubility of the coloured reaction product in the water extract; it was thought that, by carrying out the reaction in a suitable solvent, the useful range of the method would be increased.

EXPERIMENTAL

The indole used in the experimental work was prepared from a sample of commercial indole by fractionation at a pressure of 20 mm of mercury in a low-hold-up 30-plate column. The material boiling between 137° and 139° C was collected and crystallised twice from light petroleum of low boiling-point. The product was a practically odourless white crystalline solid of melting-point 53·0° C and of boiling-point 254° C.

CHOICE OF SOLVENT—

It was found that ethanol was a good solvent for the coloured compound and also for the tar oils in which indole is found, but had the disadvantage shared by other solvents that the sodium nitrate used to produce the nitrous acid was insoluble. Although organic nitrites were considered as a possible alternative, it was found that 50 per cent. aqueous ethanol gave a satisfactory compromise.

REACTION TIME—

Various amounts of the pure indole were dissolved in 50 per cent. aqueous ethanol in 100-ml calibrated flasks, and to each 0·5 ml of a 2 per cent. solution of sodium nitrite and 0·25 ml of concentrated sulphuric acid were added. The flasks were filled to the mark with 50 per cent. aqueous ethanol and shaken, and the colour produced was measured after definite intervals. The results in Table I show that the best relationship between concentration and optical density at 525 mμ is after a standing time of 2 hours. This standing time was used in subsequent experiments.

TABLE I

EFFECT OF REACTION TIME ON OPTICAL DENSITY AT 525 mμ

Standing time, hours	Optical density for—				
	0·2 mg of indole	0·6 mg of indole	1·0 mg of indole	2·0 mg of indole	2·8 mg of indole
1	0·033	0·146	0·257	0·510	0·689
1½	0·030	0·146	0·256	0·503	0·694
2	0·033	0·142	0·257	0·499	0·690
4	0·029	0·139	0·253	0·500	0·688
5	—	—	0·242	0·488	0·679
7	—	—	0·243	0·496	0·675

STABILITY OF THE COLOUR—

No difference in colour was found when it was developed in the light or the dark, or with air being bubbled through the solution.

EFFECT OF OTHER COMPOUNDS—

Of the materials likely to be present in the indole-containing tar fractions, only the homologues of indole gave any colour when treated as in the proposed method; 3-methylindole gave no colour when alone, but did so in the presence of indole. However, the boiling-points of the methylindoles identified in coal tar (2-methyl, 272° C; 3-methyl, 264° C; 7-methyl, 266° C) are sufficiently separated from that of indole (253° C) to ensure that, if the indole-containing fraction is obtained by reasonably good fractionation, no interference from the homologues is likely to occur.

METHOD

REAGENTS—

Aqueous ethanol, 50 per cent. v/v—Prepare by diluting industrial methylated spirit.

Sulphuric acid, concentrated—Analytical-reagent grade.

Sodium nitrite solution—Dissolve 2·0 g of analytical-reagent grade sodium nitrite in 100 ml of distilled water.

PROCEDURE—

Accurately weigh sufficient sample to contain between 4 and 26 mg of indole (see Note) and dissolve it in industrial methylated spirit to produce 100 ml of solution. By pipette, put 10 ml of this solution in a 100-ml calibrated flask. Add 10 ml of distilled water and nearly fill the flask with 50 per cent. aqueous ethanol. By pipette, add 0·50 ml of sodium nitrite solution and then 0·25 ml of sulphuric acid to the flask, make up to the mark with 50 per cent. aqueous ethanol and shake.

Set the flask aside for 2 hours and measure the optical density of the resulting magenta coloured solution against a blank of the reagents at a wavelength of 525 mμ or using an Ilford No. 603 filter. Read off the indole content from a calibration graph prepared by treating pure indole in a similar manner.

NOTE—

As the sample must be substantially free from the homologues of indole, they may be removed by fractionation in a column of efficiency greater than 30 theoretical plates and collection of a suitable fraction for examination.

RESULTS

The following is a selection of results determined on material containing indole—

	Indole found, %
Methylnaphthalene oil obtained from coke-oven neutral tar oil A by fractionation in a 50-plate column at a pressure of 50 mm of mercury and collection of the material boiling between 130·9° and 151·0° C	2·97
This oil with 10 per cent. of indole added and the results calculated to give the original content	2·97
Methylnaphthalene oil obtained from coke-oven neutral tar oil B by fractionation in a 50-plate column at a pressure of 100 mm of mercury and collection of the material boiling between 158·6° and 168·2° C	2·73, 2·69

A fractionation of a coke-oven drained anthracene oil in a 30-plate column at a pressure of 742 mm of mercury gave the following distribution of indole in the fractions—

Fraction number	Mid boiling-point, °C	Indole content, %	Fraction number	Mid boiling-point, °C	Indole content, %
1	211	Nil	6	240	2·87
2	215	0·15	7	250	2·00
3	219	0·29	8	259	0·85
4	233	0·84	9	265	0·56
5	237	2·06	10	270	Nil

A similar fractionation at a pressure of 50 mm of mercury of a coke-oven absorbing oil gave the following distribution of indole in the fractions—

Fraction number	Mid boiling-point, °C	Indole content, %	Fraction number	Mid boiling-point, °C	Indole content, %
12	144·3	Nil	18	156·5	14·25, 14·18
13	145·0	0·60	19	157·4	11·45, 11·64
14	145·5	1·89, 1·96	20	158·3	5·61, 5·62
15	151·9	5·28, 5·19	21	159·3	2·04, 2·01, 2·03
16	155·1	11·81, 11·92	22	160·4	1·10, 1·11
17	156·0	14·36, 14·42	23	161·6	Negligible

By using the results obtained on fractions 14 to 22, a pooled estimate of the errors of the ten replicates was calculated on a percentage basis and gave a value for the standard deviation of the method of 1·08 per cent.

We thank the Council of The Coal Tar Research Association for permission to publish this work.

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Ministry of Agriculture, Fisheries and Food and Ministry of Health

STATUTORY INSTRUMENT*

1957—No. 1066. The Colouring Matter in Food Regulations, 1957. Price 5d.

These Regulations, which came into operation on June 30th, 1957, and come into full effect by stages at later dates specified in a schedule to these Regulations, limit the colouring matters that may be used in foodstuffs to certain permitted dyes and certain other materials that are listed therein.

British Standards Institution

NEW SPECIFICATIONS†

B.S. 1428:Part A5:1957. Rapid Method Combustion Tubes (Belcher & Ingram Type). Microchemical Apparatus: Group A: Combustion Trains for the Determination of Elements. Price 3s.
B.S. 1739:1957. Filter Flasks. Price 3s.

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

† Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

Book Review

ORGANIC SYNTHESES. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 36. Editor-in-Chief: N. J. LEONARD. Pp. vi + 120. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1956. Price $3.75; 30s.

The current cosmopolitan collection comprises penta-1 : 4-diene; dichloro-1 : 1-difluoroethylene, 1-fluorohexane, toluene-*p*-sulphonic anhydride; *cis*- and *trans-cyclo*decane-1 : 2-diol; di(chloromethyl) ether, 4-iodoveratrole; propiolaldehyde, *cyclo*decanone, *cyclo*decane-1 : 2-dione, 2-hydroxy-*cyclo*decanone; α-sulphopalmitic acid, α-chlorophenylacetic acid, 2 : 4 : 6-tribromobenzoic acid, β-ethyl-β-methylglutaric acid, *o*- and *p*-nitrobenzylidene diacetates; 1 : 4-diaminobutane dihydrochloride, NN′-diethylbenzidine, N-dodecylmethylamine; N-phenylbenzamidine; N-cyano-N′-phenylurea, *p*-methoxybenzyl cyanide, N-cyanoethylaniline; diazomethane, ethyl diazoacetate; 1-*iso*thiocyanatonaphthalene, NN′-dimethylselenourea, di*cyclo*pentadienyliron (ferrocene), tetraethyltin; 2-furoic acid, 6-hydroxynicotinic acid, 4-nitro-3-picoline 1-oxide, pyrrole-2-aldehyde, tetrahydrothiophen; D-γ-gulonolactone.

As usual, some of the preparations include full details for intermediate products and some give indications of analogous compounds that have been made by the process described.

B. A. ELLIS

Publications Received

QUANTITATIVE INORGANIC ANALYSIS. By G. CHARLOT and DENISE BÉZIER. Translated by R. C. MURRAY, Ph.D. Pp. x + 691. London: Methuen & Co. Ltd.; New York: John Wiley & Sons Inc. 1957. Price 84s.

First English edition, based on the third French edition of 1955.

INTRODUCTION TO ORGANIC CHEMISTRY. By G. I. BROWN, B.A., B.Sc. Pp. 403. London, New York and Toronto: Longmans, Green & Co. Ltd. 1957. Price 16s.

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REPORT OF THE ANALYTICAL METHODS COMMITTEE: LINALOL IN ESSENTIAL OILS

THE Report prepared by the Essential Oil Sub-Committee, "The Determination of Linalol in Essential Oils," reprinted from *The Analyst*, May, 1957, **82**, 325–329, is now available from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1: price to members, 1s. 6d.; to non-members, 2s. 6d. Reports of the Analytical Methods Committee are only obtainable from the Secretary (not through Trade Agents) and remittances must accompany orders.

Erratum

APRIL (1957) ISSUE, p. 282, 2nd line from foot of text. *After* "ammonia" *add* "Finally, dilute the suspension of aluminium hydroxide to 1 litre with water."